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ABSORPTION SPECTRA OF TETRA-ALKYL AMMONIUM SALTS.

(Contributions to the Theory of Co-ordinate Linkage IX.[1])

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AND
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Received March 30, 1936.

Introduction.

IT is well known, that the conventional theory of valency as developed by Lowry, Sidgwick, a. o.[2] assumes that only certain configurations of shared electrons confer stability to a molecule. The stability of the electron octet, emphasised in analogy with the configuration of the heavier rare gases by Langmuir, was the starting point of this theory, and later on also other configurations of 12 and 16 shared electrons have been admitted. Consequently it was assumed, that molecules which do not follow this generalised octet rule, possess different kinds of non-electrovalent linkage. Thus, in the nitro-compound the two bonds in the NO_2 group shall be different and only one of them shall be true covalent bond. These considerations find their brief formulation in Sidgwick's covalency rule, which postulates the maximum number of true covalent bonds to be 4 for the second short period (Li-F), 6 for the two following short periods and 8 for the heavier atoms. A number of arguments have been put forward against this conception and a theory which ascribes chemical stability to any molecule in which the sharing electrons form completed orbitals and the molecule as such is in a term of $^1\Sigma$ type is also possible.[3] Whereas the first theory is a development of Lewis' octet rule, the second emphasises Lewis' pair-bond conception and follows more the ideas of Grimm and Sommerfeld.[4] In such a theory the maximal number of (covalent or electrovalent) bonds always equals the number of outside electrons of the atom and different types of non-electrovalent bonds are not necessary. Thus nitrogen in nitro-compounds or in N_2O_5 is simply penta-covalent, because it possesses 5 valence electrons. The obvious differences of analogous atoms of the different periods find their explanation in energetical considerations. The non-existence of NCl_5 together with the existence of PCl_5 is then due to the

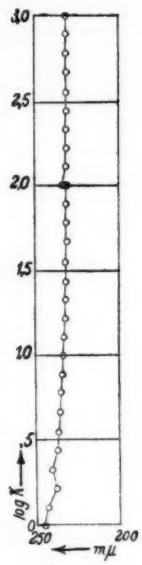

FIG. 1.

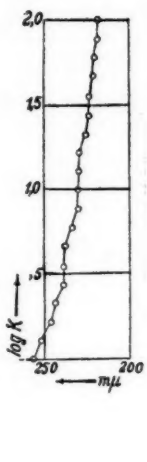

FIG. 2.

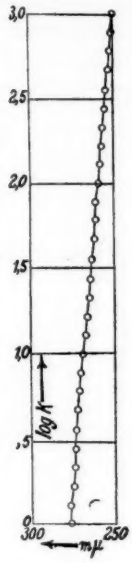

FIG. 3.

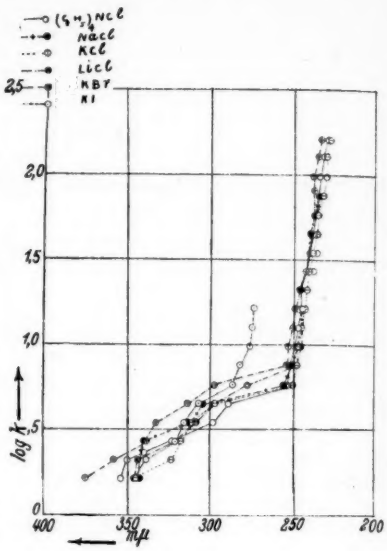

FIG. 4.

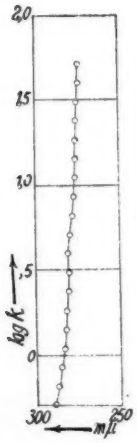

FIG. 5.

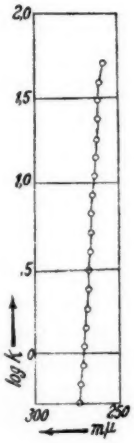

FIG. 6.

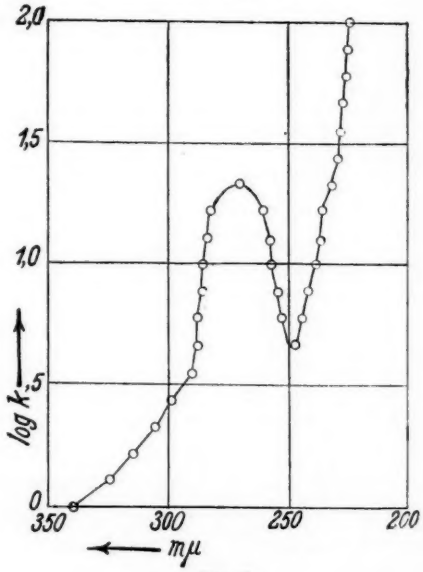

FIG. 7.

FIG. 1. $(CH_3)_4$ NCl.
FIG. 2. $(CH_3)_4$ NBr.
FIG. 3. $(CH_3)_4$ NI.
FIG. 4. $(C_2H_5)_4$ NCl in different solvents.
FIG. 5. $(C_2H_5)_4$ NBr.
FIG. 6. $(C_2H_5)_4$ NI.
FIG. 7. $(C_3H_7)_4$ NCl.

higher energy of excitation necessary to split the s^2 group of electrons of the nitrogen atom. It should be mentioned in this connection, that during the preparation of various nitrogen fluorides Ruff and his collaborators[5] have found quite definite evidence of the existence of NF_5. Sometime ago Ebert and Lange[6] in the course of cryoscopical measurements found certain deviations from the behaviour, expected by the Debye-Hueckel theory in the case of strong solutions of certain tetra-alkyl ammonium halides, which clearly show, that some of these salts do not dissociate completely in water. The effect becomes more marked with the increase in mass of the organic

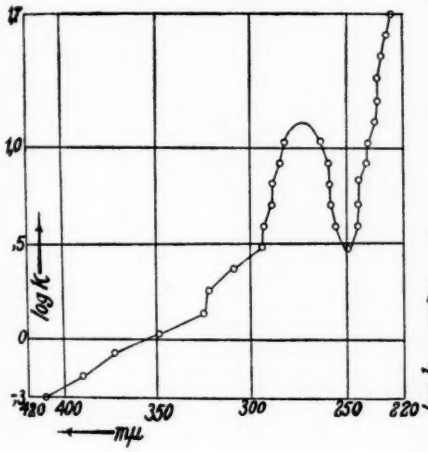

FIG. 8. $(C_3H_7)_4$ NBr.

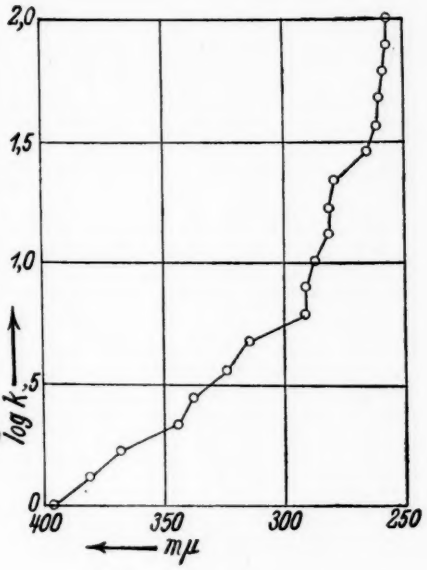

FIG. 9. $(C_3H_7)_4$ NI.

radical and the substitution of halogens possessing lower electronic affinity. These measurements, however, are not qualified to distinguish between the non-dissociated molecules with a true covalent nitrogen-halogen bond, and pairs of ions, *i.e.*, non-dissociated but still electrovalent molecules kept together by electrostatic forces, or the effect of formation of association of the ions themselves or of ions and water molecules. For the theories of valency, however, it would be of great interest indeed, to find out, if in solutions of tetra-alkyl ammonium halides there is really an equilibrium between electrovalent and covalent molecules, because it would contradict

the first and confirm the second of the above theories. Even if the percentage of covalent molecules is small, the existence of molecules in which nitrogen possesses five single covalent links would be of interest. Ebert and Lange emphasise, however, that it will not be possible to interpret their results by the introduction of one kind of interaction only and therefore it could be hoped for, that investigations of the absorption spectra

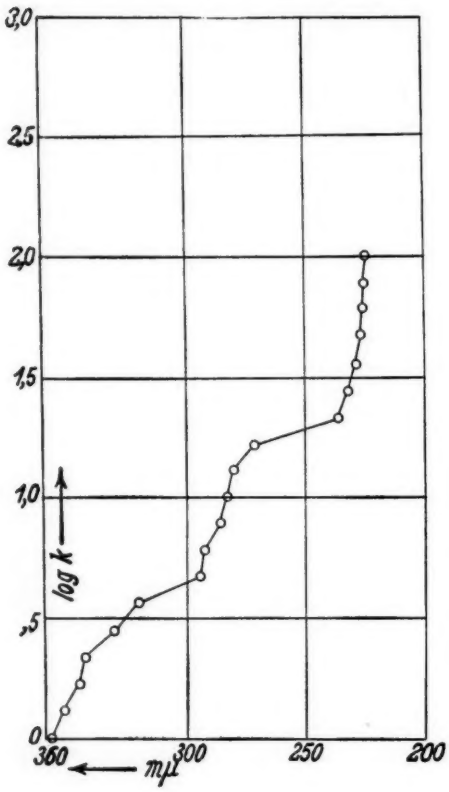

FIG. 10. $(C_4H_9)_4$ NBr.

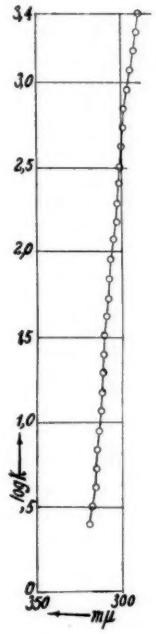

FIG. 11. $(C_4H_9)_4$ NI.

may contribute at the same time to the question of the structure of highly concentrated solutions of electrolytes in water. From these points of view we have undertaken an investigation of the absorption spectra of these salts in solutions of high concentrations ($c = 1.0$ to $0.1\ m$) as well as in those of low concentrations ($c = 0.01$ to $0.00001\ m$).

Solutions of High Concentration.

For the measurements of the absorption spectra we employed at first a method, used in this laboratory and, besides later minor improvements, originally described elsewhere.[7] As in many other similar methods, twin spectra of the solution and (with reduced illumination) of the solvent are taken with different concentrations and absorbing layers, and the wavelengths of equal intensity observed visually. The introduction of a discharge tube with stagnant gas, giving the continuous hydrogen spectrum,

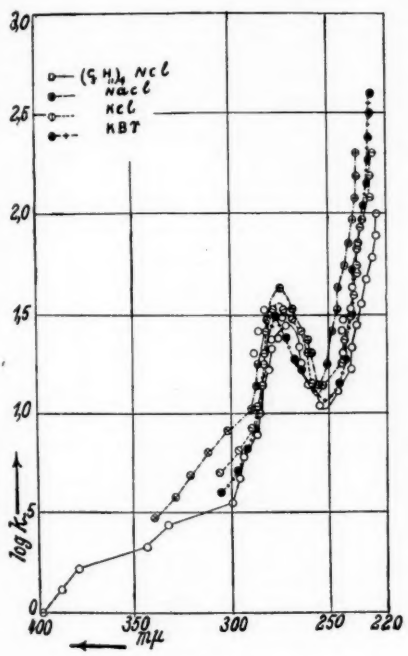

FIG. 12.

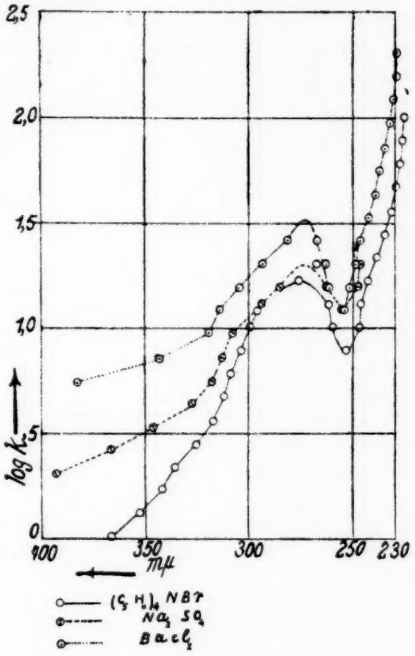

FIG. 13.

FIG. 12. $(C_5H_{11})_4$ NCl (iso) in different solvents.

FIG. 13. $(C_5H_{11})_4$ NBr (iso) in different solvents.

makes certain simplifications possible. The results, obtained with this method, indicated certain deviations from Beer-Lambert law and have been supplemented by precision measurements, in which the intensities of twin spectra of solution and solvent with equal illumination were directly measured by means of a recording microphotometer.

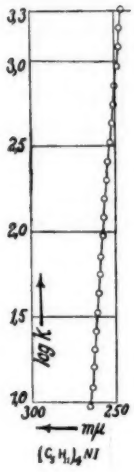

FIG. 14

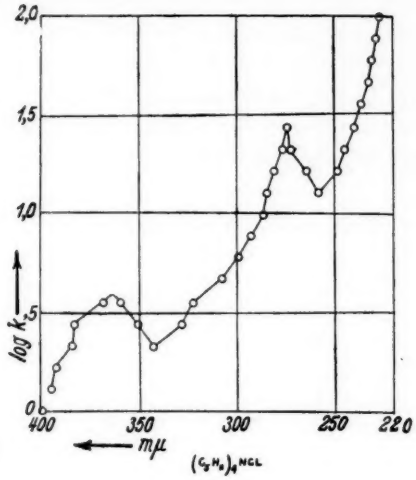

FIG. 15.

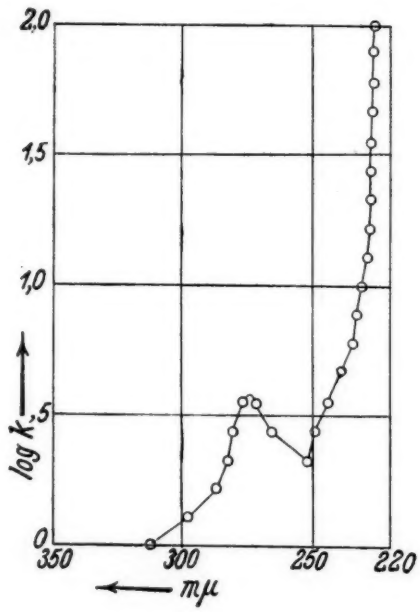

FIG. 16.

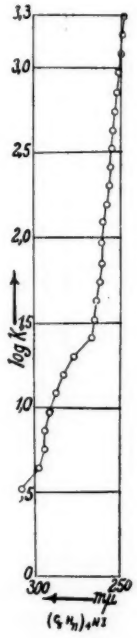

FIG. 17.

FIG. 14. $(C_5H_{11})_4$ NI (iso).
FIG. 15. $(C_5H_{11})_4$ NCl (Normal).
FIG. 16. (C_5H_{11}) NBr (Normal).
FIG. 17. $(C_5H_{11})_4$ NI (Normal).

The results of the first series are given in the diagrams of figures 1 to 17. Here the absorption coefficient k is defined by the equation $I = I_0 . 10^{-kcd}$, I_0 and I being the intensities of light, entering the medium and emerging from it, c and d stand for the concentration of the solution and the thickness of the layer. The concentration of these solutions was of the order 1.0 to 0.1 *m*. The absorption curves are shown in figures 1 to 17.

TABLE I.

Maxima of Salts R_4 NX.

R =	Chloride		Bromide		Iodide	
	Ist Max. $\lambda(m\mu)$ log K	II Max. $\lambda(m\mu)$ log K	Ist Max. $\lambda(m\mu)$ log K	II Max. $\lambda(m\mu)$ log K	Ist Max. $\lambda(m\mu)$ log K	II Max. $\lambda(m\mu)$ log K
CH_3	..	..	..	..	..	..
Max. conc.	1 *m*		0·1 *m*		0·2 *m*	
C_2H_5	diffuse	diffuse	..	..	..	..
Max. conc.	0·2 *m*		0·2 *m*		0·2 *m*	
C_3H_7		270 1·3	~320 0·25	270 1·1	~315 ~0·6	~280 ~1·1
Max. conc.	0·1 *m*		0·2 *m*		0·1 *m*	
n–C_4H_9			320 0·55	270 1·2		
Max. conc.			0·1 *m*			
n=C_5H_{11}	364 0·55	274 1·4		274 0·6		~270 ~0·4
Max. conc.	0·1 *m*			0·1 *m*	0·005 *m*	
i=C_5H_{11}	~360 0·35	272 1·4	~330 0·15	277 1·2	..	..
Max. conc.	0·1 *m*		0·1 *m*		0·005 *m*	

From the comparison of the curves it will be seen that from $R = C_3H_7$ onwards selective absorption obtains. Mostly we have one well-defined and sharp maximum at about 270 $m\mu$ and another, more diffuse one preceding it at about 310 $m\mu$. The first one is always sharp. In $(C_4H_9)_4NI$ it is apparently only superimposed on the ascent of the band which is exhibited by the iodine ion at 227 $m\mu$. For such diffuse maxima we have taken the turning points of the curves as maxima and have deducted the probable value of the short wave ascent from its k value. The results are

summarised in Table I. It is interesting to note, that in general the selective maxima occur with heavier radicals, but in each series the chloride appears to develop them stronger than the bromide or iodide. In $(C_5H_{11})_4$ NCl, *i.e.*, the heaviest of the chlorides, the maximum at 310 $m\mu$ is just indicated, but a further maximum at about 365 $m\mu$ is developed, which could not be found in the other curves. This latter one appears quite distinct in the *n*-molecule and is still indicated in the iso-compound. In the series with $R = C_2H_5$, the chloride shows already indications of the maxima, even if only diffuse and at low values of log k, the bromide and iodide show a continuous end absorption only, like the salts with $R = CH_3$. In the series with $R = C_3H_9$ we find a slight decrease of the log k values in the same directions, which is more strongly marked in the series with $R = n - C_5H_{11}$, where the log k values of the main maximum at 274 $m\mu$ decreases from 1.4 in the chloride to 0.6 in the bromide. The corresponding figures for the iso-forms are 1.4 for Cl, and 1.2 for Br.

Since the main maximum possesses about the same wave-length independent of X being Cl, Br or I, it seems reasonable to assume, that this selective absorption belongs essentially to hydrated R_4N^+ ions. On the other hand, the maxima appear only with heavier radicals, and it contradicts every experience to assume that the selective absorption if it belongs to the C – N link, should obtain only when longer chains are attached to the C atom. Furthermore, if this absorption would be due to the R_4N^+ ions alone, the differences in intensity (log k) values between chlorides, bromides and iodides and those between the normal and iso forms of (C_5H_{11}) NBr and (C_5H_{11}) NI could not be explained.

Further corroboration is furnished by the optical behaviour of these salts in the presence of foreign salts. The solution of $(C_2H_5)_4$ NCl, where the maxima are still found indistinct at low values of k, shows, that all curves in the presence of foreign ions are shifted in the same sense against the curve in water; only the absorption coefficient is increased and the curves are slightly shifted towards red. Those in solutions of the three chlorides LiCl, NaCl, and KCl are close together, while those in solutions of KBr and KI show stronger effects. (*Cf.* Fig. 4.)

We have then measured solutions of $(C_5H_{11})_4$ NCl, where the maximum is more distinct than in the former ones, in the presence of NaCl, KCl, and KBr and of $(C_5H_{11})_4$ NBr in the presence of Na_2SO_4 and $BaCl_2$. It can be seen (Figs. 12 and 13) that again the curves of the former salt in solutions of NaCl and KCl are close together, whereas the log k value reaches appreciably higher values and the curve broadens in the presence of the Br ion. Here the influence of the negative ion is clear. The changes of the

absorption coefficient to our mind are more important than those of wave-length. Table II gives the wave-lengths in $m\mu$ of the maxima obtained.

TABLE II.

Chloride		Bromide	
In water	272	In water	277
In water + NaCl	276	In water + Na_2SO_4	275
In water + KCl	275·5	In water + $BaCl_2$	275
In water + KBr	275		

It does not appear to us to be impossible that the differences of wave-length are below the sensitivity of the experimental method and that these experiments do not allow us to distinguish accurately between the wave-length of the maxima in the presence of foreign ions. We cannot be certain whether the differences between 276 and 275 $m\mu$ are real. It can be seen, however, that the maximum of the bromide, compared with that of the chloride, in water without additional salts, is certainly shifted towards red and that, independent of this, the maximum obtains a position at about 275 to 276 $m\mu$ in the presence of foreign salts.

Some Remarks on Optical Effects in Concentrated Solutions of Strong Electrolytes.

The interpretation of these effects leads us to the question of the structure of solutions of strong electrolytes at higher concentrations. It is well known, that the theory of Debye-Hueckel still needs further development to explain the behaviour of such highly concentrated solutions, c being about 1 to 0.01 m. From the point of view of the optical behaviour of strong electrolytes and particularly as regards absorption spectra the problems connected with this question have been discussed by Scheibe[8], von Halban,[9] and Fromherz,[10] and their collaborators. Scheibe and Fromherz interpret the observed changes in the selective absorption of various ions due to the presence of foreign salts, in terms of changes in the deformation of the absorbing ions in the unlike field of the anti-ions, which may form a surrounding atmosphere of opposite charge or may form pairs with the absorbing ions according to the conceptions put forward by Bjerrum[11] to adapt the Debye-Hueckel theory of strong electrolytes to higher concentrations. Von Halban and his collaborators have on the other hand always

maintained that other influences exist too and in the last paper of Kortuem[12] not the interaction between oppositely charged ions but the effects of hydration and dehydration, or, in other words, the interaction of the absorbing ion with the dipole molecules of the solvent are held mainly responsible for the observed changes of the absorption curve.

To our mind it is evident, that both effects play a rôle and that the observed changes as for instance those of the absorption of R_4N^+ ions above cannot be expressed in terms of one parameter only. A simple reference to the properties (hydration, polarisability, or diameter) of the anti-ions alone is not sufficient and the influence of the ions of like charge is certainly present here as well as in other instances as shown in previous papers of this series. We have mentioned above that also Ebert and Lange[6] have come to a similar conclusion from cryoscopical measurements and a number of authors have already emphasised that the structure of solutions of electrolytes at higher concentrations is rather a complex phenomenon. Special mention may be made of the measurements of Darmois[13] on the optical activity of tartrates in the presence of neutral salts, which have led him to the assumption, that dehydration and deformation influence the optical activity in the opposite way.

But the conclusion that the interaction effects in higher concentrated solutions of strong electrolytes are of a complicated nature and that various different effects exist side by side, is about the only one which in the present moment can be made with certainty. How difficult it is, to predict the result of any one of the various possible effects, say of hydration or deformation of the absorbing ion, on its selective absorption, will be seen, when the Franck-Condon diagram which has already served as a useful instrument in so many discussions on the absorption and emission of isolated molecules in the vapour state, is made the basis of discussion.

The three-dimensional Franck-Condon diagram of a molecule $A^+(BC)^-$ — we may think of KOH—may be represented schematically in a simplified manner in Fig. 18. The ground level of the ion $(BC)^-$ may be formed by the union of $B + C^-$ and the level of these separated constituents $A^+ + B + C^-$ will be above that of the neutral atoms $A + B + C$, since generally the electronic affinity of C will be smaller than the ionisation potential of A. In any case we will find, in analogy to diatomic and polyatomic molecules in the vapour states, a number of repulsive curves and an absorption of light, *i.e.*, a transition from the ground level to any one of them, will produce a region of continuous selective absorption which may be correlated to a process of photo-dissociation or to the tearing off of the superfluous electron of the negative ion in solution, the latter spectra may also be due to the

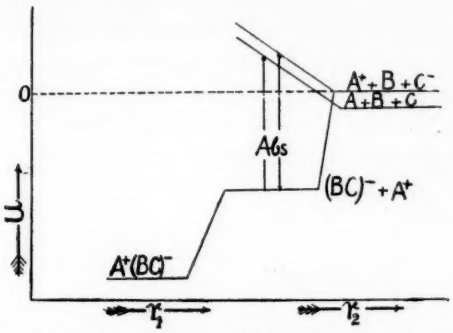

FIG. 18. Scheme K of Franck-Condon Diagram of a Triatomic Salt.

transition of the electron to a molecule of the solvent under formation of *e.g.*, OH^- ions as shown by Franck and Haber[14] but such complication shall not be considered here. It is, however, evident, that the absorption of light is represented by the upper part of the energy diagram, which belongs essentially to the $(BC)^-$ ions, representing its dissociation or formation, in which the A^+ ion does not take any part, but is considered to be at infinite distance, in the level of the separated constituents $B + C^-$ as well as in that of the ground level of the ion $(BC)^-$. The formation of $A^+(BC)^-$ originates from the latter one and is represented in the lower part of the diagram. If we consider now those conceptions which assume in higher concentrated solutions the formation of associations of the A^+ and the $(BC)^-$ ions, either as atmospheres of oppositely charged ions or particularly as pairs of unlike ions, this will be a process in which A^+ ions are not any longer at an infinite distance from the $(BC)^-$ ions and which is therefore connected with this lower part of the energy diagram. Any change due to deformation of the ion $(BC)^-$ in its unexcited level will therefore have quite different effects on the two parts of the diagram, since this level forms the lower state for the representation of the selective absorption and the upper one for the formation of undissociated ions $A^+(BC)^-$. According to Kortuem's measurements the absorption spectrum of dinitrophenol does not undergo any change in concentrations of medium strength (up to 0.01 *m*) in which activity coefficients, conductivity and similar observations indicate already deviations from the theory of Debye-Hueckel. For still higher concentrations he finds changes of the optical properties, but these do not go parallel with those formed by means of thermodynamical and electrochemical measurements. He concludes that the interaction of the absorbing ion with the molecules of the solvent is the essential effect, and not that between the ions of opposite charge. From the above diagram it is evident, that this

is by no means conclusive for the reason, that absorption and approach of unlike ions belong to quite different parts of the energy diagram.

In Fig. 19*a* the lower part of this diagram has been used to represent the process of hydration of the system $A^+ (BC)^-$. In the process of hydration or solvation a certain amount of energy is liberated, which has to be added for all internuclear distances and brings about a lower position of

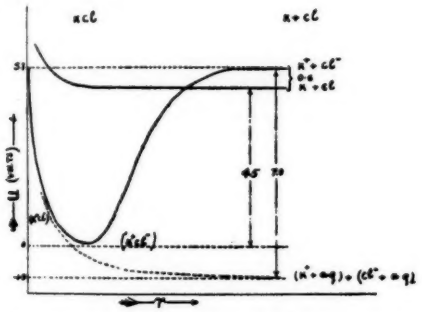

FIG. 19*a*. Franck-Condon Diagram of a Triatomic Salt. 1st Part.

the U : *r* curve. If the undissociated molecule is an electrovalent one* the hydration energy of the two ions together represents naturally a much bigger amount than that of the undissociated molecule because the number of water molecules held by the two separate ions and the force by which they are bound to them is much larger than for the neutralised molecule itself. This is evident for those simpler diatomic salts for which all figures, *i.e.*, ionisation potential, electronic affinity and energy of hydration of the two ions and the heat of formation of the gaseous compound are known; Potassium chloride may serve as an example[15] and its Franck-Condon diagram is given in figure 19*b*. In KCl the level of the separated ions is about half a volt above that of the separated neutral and unexcited atoms. The energy of hydration is known to be 73 k. cal./mol. for K^+ and 89 k. cal./mol. for Cl^- and hence the level of the separated ions in the state of hydration lies about 7 volts below that of the unhydrated ones or about 6.5 volts below that of the separated neutral atoms. The ground level of the undissociated gaseous ionic molecule (K^+Cl^-) lies about 103 k. cal. or 4.5 volts below that of the neutral atoms or still about 2 volts above that of the hydrated ions and the energy of hydration for this form will be very small,

* The term electrovalent is used, when the adiabatic excitation of the vibrational levels of the ground state dissociates a molecule into ions, and a molecule is called covalent, when the adiabatic dissociation of its ground state involves neutral atoms.

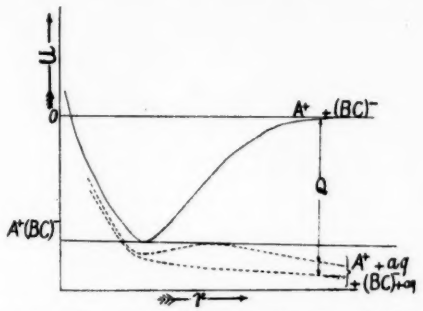

FIG. 19*b*. Franck-Condon Diagram of KCl.

because the opposite charges cancel each other. The fact, that KCl dissociates in aqueous solutions shows already that the hydration energy of the undissociated molecule is less than this difference of about 40 k. cal./mol. and that the level of the separated hydrated ions has become the lowest one of the system. The great difference of the hydration energy of the two systems $K^+ + Cl^-$ and (K^+Cl^-) turns the $U : r$ curve into a repulsive one and as a matter of fact the above is only a description of the process of hydrolytic dissociation by means of the Franck-Condon diagram. Similar repulsive curves have to be expected quite generally for molecules dissociating into ions and even if the electrovalent curve of the non-hydrated molecule is not that of the ground level but near to it, that involving the separated hydrated ions may intersect the potential curve of the ground level and may become the lowest one of the system,[14] as in AgCl.

Two conclusions become evident at once from this description by means of the $U : r$ curves. In Fig. 19*a* the lowest dotted curve represents the dissociation process due to the difference of hydration energy and is shown here as a repulsive curve. If, however, the concentration is increased and the number of water molecules at the disposal of the individual molecule $A^+(BC)^-$ is appreciably decreased, the energy of hydration decreases too, and the original curve of the gaseous state being the limiting case in which the hydration energy vanishes, higher curves of the hydrated system should be expected, showing a labile minimum in the neighbourhood of the internuclear distance of the gaseous molecule. An attempt to draw such a curve is shown by the upper dotted curve of Fig. 19 *a*, but in any case such curves with a slight minimum must come into existence if the additional energy of hydration is sufficiently decreased. Such a minimum may be taken as the energetical representation of Bjerrum's pairs of ions.

Secondly, this diagram of the position of the electronic terms of the system $A^+(BC)^-$, depending on r, does not give any indication as to the change of the selective absorption of the ion $(BC)^-$. In this description r represents the distance between the cation and the (BC) anion, the latter one is taken as an entity and the change of the relative position of its own electronic terms, on which its optical properties depend, does not appear at all, and has no direct connection with the dissociation process of the cation and the anion. Hence one set of observations like electrical conductivity, concerning the system $A^+ + (BC)^-$, may well indicate the existence of non-dissociated ions in such concentrations, in which absorption measurements show that the relative position of the terms of the $(BC)^-$ ion itself has not yet changed.

The change of wave-length as produced by the addition of hydration energy to the system depends again on whether the hydration of the undissociated ion $(BC)^-$ or that of the separated system $B + C^-$ is the greater. Fig. 20 represents the case in which the separated system $B + C^-$ gains more energy than the complex ion $(BC)^-$. The change in wave-length pro-

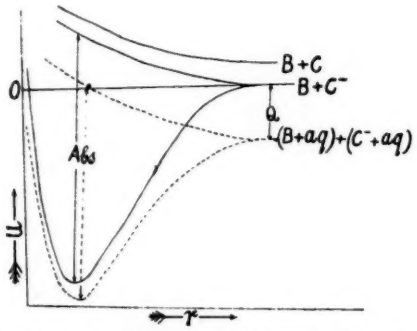

FIG. 20. Franck-Condon Diagram of Triatomic Salt. 2nd Part.

duced in this way is always a small effect and we may therefore assume that the general form of the potential curve remains unchanged and that excited states become less and less affected. If then the energy difference between the unhydrated system (full lines) and the hydrated one (broken lines) is bigger on the right-hand side for the separated constituents than on the left-hand side for the completed ion, the effect of such an increase of energy will be to shift the region of selective absorption slightly towards red, and the dehydrating effect of the presence of ions of like or unlike charge in the solution will shift the maximum towards shorter wave-length. This effect seems to exist in certain of Warner's complex salts, investigated

earlier,[1] *e.g.*, when the absorption curves of $Na_3[RhCl_6]$ does not differ, in the presence of NaCl and KCl but is shifted towards the ultra-violet when the additional salt is replaced by Na_2SO_4. Indeed it is very plausible to assume that the hydration energy of such a complex ion is less than the sum of those of its constituent ions and the characteristic influence of the ions of like charge can be explained in this way quite well. When, however, the hydration energy gained by the separated system happens to be smaller than that of the united ion, just the reverse effect has to be expected, and in cases like the R_4N^+ ions it is not easy to decide, which hydration energy may be the larger one. It could be argued that the field in the neighbourhood of a completed ion will always be smaller because the charge is the same as in the separated constituents, while the radius is bigger. But this will not be true always ; the charge is not evenly distributed but localised in the molecule and new dipole moments may be produced in the N — R bonds. More often, however, the hydration energy of the separated system should be bigger and therefore hydration should produce a shift towards longer, and dehydration by the neutral salts added to an aqueous solution, towards shorter wave-lengths. Such considerations seem to explain also most of the effects observed on the absorption curves of organic molecules in different solvents.

Superimposed on this effect is that of the deformation of the absorbing ion by the field of an added foreign ion. Whereas the first effect may be produced by ions as well of like and of unlike charge, this second effect may be expected to be characteristic for the ion of opposite charge, because such ions will be found in the neighbourhood of the absorbing ion or will pair with it at stronger concentrations. Not very much can be said about the result of such a deformation on the absorption itself. In the Franck-Condon diagram such an effect will produce a change in the internuclear distance of the minimum position and, furthermore, the energy of dissociation and the whole force system and the slope of the curves will be changed. In this connection, however, the rule of Fajans and Joos[16] may be mentioned, according to which the electronic configuration of a cation will be loosened while that of the anion consolidated by the mutual deforming influence. This rule has been confirmed by many observations on monoatomic ions. We will assume that it holds also for more complex ions, because at least for the anions there should not be much difference. This is not so certain for cations, because the complex cations possess outside electrons, which the monoatomic ones mostly have lost. We remember again, that the effects in question are only slight, and we assume therefore that the changes on the potential curves are slight too and may be neglected increasingly

for the higher terms. In this case we expect that the absorption maximum of a cation will be shifted towards longer wave-lengths, that of an anion towards shorter wave-lengths as a result of the deforming influence of an ion of opposite charge. In the Franck-Condon diagram, the consolidation of the electronic configuration may be compared to the normal case of band spectroscopy in which the ground level possesses a smaller r, larger vibrational frequency and larger energy of dissociation than the excited level and the loosening of the electronic structure to the reverse, normal case. The ground level corresponds to the ground level of the undeformed, the excited to the ground state of the deformed molecule. If the repulsive curve does not suffer more than very slight changes, the energy difference between that and the ground level will be decreased in the former and increased in the latter case. Such a conception appears well qualified to explain many effects observed on the absorption curves of inorganic ions and is more or less identical with certain conceptions, developed by Scheibe and his collaborators.

There is, however, still another effect possible already discussed by Fromherz. These two cases of deformation, essentially a decrease or increase of the polarisability, may effect mainly the absorption coefficient and not the wave-length. According to the theory of dispersion the polarisibility is directly proportional to the absorption coefficient and inversely proportional to the frequency, and anions in the field of deforming cations can then show a decrease in the absorption coefficient, cations in the field of deforming anions an increase.

We have seen, that the selective absorption of the tetra-alkyl ammonium salts appears gradually with increasing weight of the radical and is not identical in n and i forms. This effect appears to be due to the deformation of the ion in the field of the hydrating water molecules, which is different according to the size and arrangement of the radical and therefore we have ascribed the selective absorption to the hydrated ions. The dehydrating effect of Cl^- is bigger than that of Br^- and consequently the larger deformation in $(C_5H_{11})_4NBr$ produces a maximum at a slightly longer wave-length than in $(C_5H_{11})_4NCl$. At the same time there is a marked difference of intensity between chlorides, bromides, and iodides, the k values of the chlorides being the greater one. This effect cannot be ascribed to the dehydrating influence of the anion as the Cl^- ion is the more hydrated and hence the more dehydrating one, and this effect has to be interpreted as a true deformation of the cation by the anion. These absorptions concern mainly, but not entirely, the value of the absorption coefficient and come therefore under the last of the above headings. But

it is clear, that both effects, the interaction with the molecules of the solvent and with the oppositely charged ions have to be considered.

This is corroborated by the optical effects, produced by foreign ions. All three curves of $(C_5H_{11})_4$ NCl, in the presence of NaCl, KCl and KBr lie at longer wave-lengths than that in water only, the KCl and NaCl curve closer together, that in a KBr solution more apart. This indicates the deforming influence of the anion on the cation and the effect of the Br^- ion is probably slightly the stronger because the radius of the hydrated Br^- ion is smaller than that of the hydrated Cl^- ion and it can approach the cation more closely. Again the dehydrating effect of the positive ion can be seen from the curve of the bromide in a solution of $BaCl_2$, which is much above that in Na_2SO_4, but only as far as the absorption coefficient is concerned.

The curves of $(C_2H_5)_4$ NCl in the presence of foreign salts show exactly the same behaviour. On account of the deforming influence of the anion on the R_4N^+ ion, all curves are slightly shifted towards the red and have increased k values. Those due to the Cl^- ion are all closer together, than the other ones, the effect being more marked in the order $Cl^- < Br^- < I^-$, *i.e.*, in the order in which the radius of the hydrated halogen ions decreases and the minimum distance of approach therefore decreases too.

These few remarks will be sufficient to show, that the effect of both kinds of interaction have to be considered and that the long wave-length maxima are due to the hydrated R_4N^+ ions.

Measurements on the Absorption Band of the Iodine Ion, at Low Concentrations.

Further experiments concern such solutions of low concentrations for which Beer's Law has been found to be rigorously valid in many cases and particularly for the bands of the iodine ion. This gives us an opportunity to ascertain whether there exist indications of a true covalent nitrogen-halogen bond. This was done by a precision method, as mentioned above, since the percentage of such covalent molecules is necessarily very small. A sample microphotogram of two solutions of $(C_5H_{11})_4$ NBr, taken on the same plate together with that of the source of light through distilled water only is shown in Fig. 21, Plate XXII. In each case the exposure time is exactly equal, the one solution, however, has a strength of $\frac{M}{10}$ in an absorption cell of 9.99 mm. length, whereas the other solution had a strength of $\frac{m}{100}$ and the leng h of the absorption cell was 99.983 mm. It can be seen, that the absorption curves join exactly on the long wave side, showing that the

illumination was indeed identical and no errors due to slight changes in the adjustment have occurred. In the region of the selective absorption itself, however, the curve of the more concentrated solution lies definitely slightly below that of the more diluted one. In spite of the same number of molecules being present the number of absorbing centres has decreased, indicating that the number of association complexes, formed by the R_4N^+ ion, decreases with increasing concentration.

From the discussion above, it is obvious that different interpretations of these maxima between 300 and 270 $m\mu$ are possible, and therefore such deviations from Beer's Law even without shift of wave-length are not conclusive for the existence of a true covalent bond. They may be taken as indicating the existence of still another form of association, but they do not give a definite answer as to the nature of such a second not dissociated form. There is, however, another possibility definitely to test whether this second associated form really is identical with a molecule, which possesses a covalent nitrogen-halogen bond covalent. Scheibe[8] has found two bands belonging to the iodine ion, with maxima at about 226 and 192 $m\mu$. There is no doubt, that these two bands belong to the negatively charged iodine ion; the energetical difference of 7900 cm.$^{-1}$ of the two bands agrees with the doublet separation of the ^2P ground level of the iodine atom of 7600 cm.$^{-1}$ and these two regions of absorption have been correlated to photo-dissociation processes $I^- + h\nu = e + I\,(^2P_{\frac{3}{2}})$ and $I^- + h\nu = e + I\,(^2P_{\frac{1}{2}})$ and it is probable that the electron forms OH ions subsequently. Fig. 22 shows the first of these two bands in a solution of concentration of $(CH_3)_4NI$. The photometer curve indicates that the absorption of the iodine ion persists in solutions of tetra-alkyl ammonium iodides. Its maximum was measured at 227 $m\mu$.

We have then compared the absorption of different concentrations. In order to increase the accuracy of the photometric measurements the exposure time was arranged in such a way, that all plates were not too dark but the spectra were just slightly grey; accordingly the maxima themselves are not very pronounced on these records. Fig. 23 shows the absorption of two solutions of (C_5H_{11}) NI, firstly with $= \frac{m}{10{,}000}$ and $d = 10$ mm., secondly with $= \frac{m}{2{,}000}$ and $d = 2$ mm. Again the absorption curve of the more concentrated solution lies definitely below that of the more diluted one. In Fig. 24 the first of these two solutions is replaced by an even more diluted one, $= \frac{M}{1{,}00{,}000}$ and $d = 100$ mm. it can be seen that the difference between the curves is still increased. Again the curves join exactly in the unabsorbed

region, showing that adjustment and illumination did not change. All curves have been taken from the same plate, to avoid possible differences of blackening due to developing. Similar results obtain also with lighter salts, *e.g.*, $(CH_3)_4$ NI. The effect is certainly small and we do not intend to work it out quantitatively. But there is no doubt, that qualitatively the concentration of the iodine *ion* decreases with increasing concentration.

Scheibe and Fromherz and their collaborators have shown in a number of investigations, that for the maxima of the iodine ion at such low concentrations as used here, Beer's Law is rigorously valid. Moreover, at low concentrations from 0.001 onwards also other optical measurements of absorption spectra, refractive index, etc., as well as thermo-dynamical and electrochemical measurements have shown, that the properties of the ions are independent of concentrations. Furthermore, whenever with much higher concentrations a change of the k values of the bands of I^- has been observed it was accompanied by a change in wave-length, whereas in our measurements the wave-length of the maximum remains constant and the absorption coefficient alone is changed.

The optical constancy of these bands is very well known indeed and since the same amount of iodine was present in these solutions and since this particular band is characteristic for the negative iodine ion there appears to be only one possible interpretation, namely, that a certain percentage of iodine ions has lost its ionic character. This evidently means, that there exists still another form of the tetra-alkyl ammonium iodides, with which the dissociated molecules of the salt are in equilibrium, in which they possess a true covalent N—I bond, and that nitrogen under favourable conditions can be penta-covalent in agreement with a pair-bond theory of valency.

The solutions of tetra-alkyl ammonium halides are apparently a mixture of three different forms. The bulk of a solution of R_4 NX in water at low concentration is dissociated in R_4N^+ and X^- ions, as long as R is CH_3 or C_2H_5. When R becomes heavier, association complexes are formed by the hydrated ions, in which also X plays a rôle (pairs of ions ?), and the percentage of such complexes appears to be comparatively large at concentrations of 1 to 0.1 *m*. At the same time at least the iodides are in equilibrium with a small percentage of a third form which is characterised by a covalent bond between nitrogen and iodine.

In previous papers of this series[1,17] we have already come to the conclusion, that the term 'complex salt' now-a-days is used for quite different classes of molecules. We have defined as "genuine complex salts" such compounds, in which the complex ion preserves its individual identity as such also in solution and in which physical measurements like absorption

spectra or Raman effect indicate some kind of true chemical, non-electrostatical linkage between the central ion and those molecules or ions which surround it. This definition excluded all cases of crystal water, or crystal alcohol, etc., where a definite co-ordination number is produced not by the number of co-ordinate bonds but by the geometrical properties of the crystal. It excludes furthermore cases like the hydrated ions of the transition elements, in which the absorption spectrum indicates that the water molecules are held as loose associations on account of electrostatic forces. It is interesting to note, that Day, Hughes, Ingold and Wilson[18] on account of quite different observations have come to the same conclusion in the latter case.

But also in the class of genuine complex salts the co-ordinate bond appears to be the representation of quite different physical mechanisms in various cases. The absorption spectra of tetra-alkyl ammonium salts do not show any phenomenon which could not be attributed to ordinary covalent bonds between carbon and nitrogen. On the contrary, the transition to covalency of the nitrogen-halogen bond, which was observed for a small percentage in low concentrations directly contradicts the conception of the co-ordinate bond as originally developed by Werner. The most simple and straightforward description of the mechanism of linkage appears to be to attribute 5 covalent bonds to the N atom on account of its 5 outside electrons $2s^2\ 2p^3$. It is clear that among the five bonds that between nitrogen and halogen will be much more polarised than the four nitrogen-carbon bonds, and hence this bond will be the one which becomes electrovalent under the influence of additional outside energies like that of hydration or of the crystal lattice. If this is so, the tetra-alkyl ammonium salts do not belong to the same class as for instance the hexa cyanides of Co, but have to be considered as simple derivatives of pentavalent nitrogen. To our mind this conclusion is strongly corroborated by the fact, that, according to their absorption spectra,[19] also inorganic nitrates are covalently bound in the vapour state and exhibit an electrovalent bond only in solution. The different chemical behaviours of the fifth bond of nitrogen appear to find its explanation more by considerations of bond energies and polarisation than by the assumption of a special quality of this bond.

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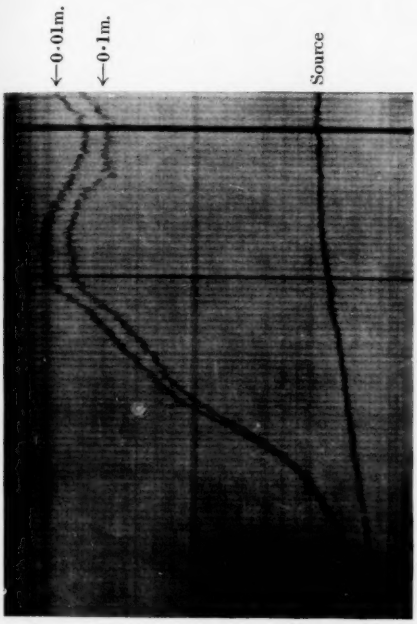


FIG. 21. Photom. Record, (C_5H_{11}) NBr.

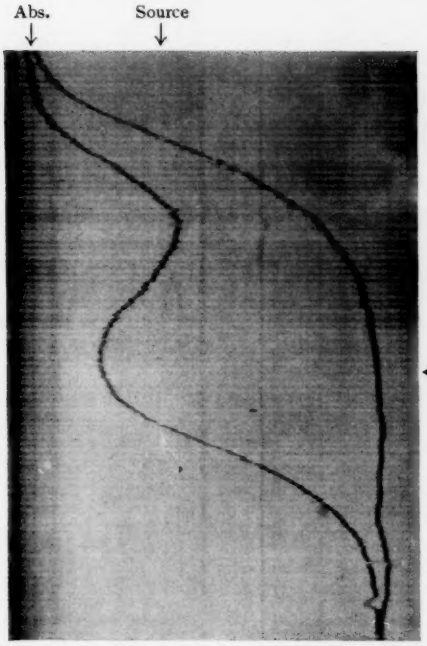


FIG. 22. Photom. Record, $(CH_3)_4$ NI absorption.

FIG. 23. Photom. Record, $(C_5H_{11})_4$ NI.

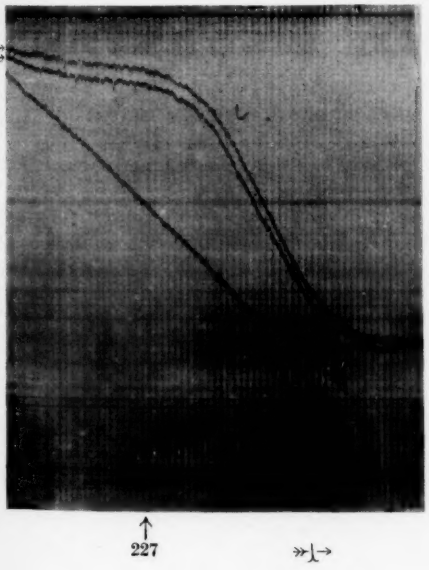
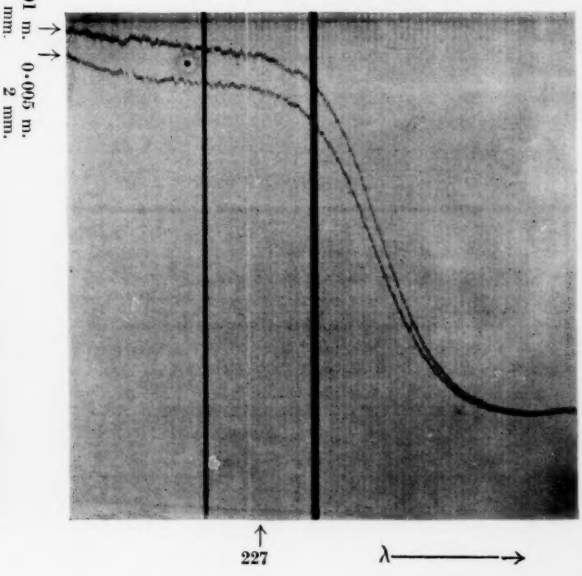


FIG. 24. Photom. Record, $(C_5H_{11})_4$ NI.



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EXPLANATION OF FIGURES IN THE PLATE.

FIG. 21. Photometer record of $(C_5H_{11})_4$ NBr solution. 0.1 m. and 9.99 mm., 0.01 m. and 99.98 mm.

FIG. 22. Photometer record of $(CH_3)_4$ NI solution.

FIG. 23. Photometer record of $(C_5H_{11})_4$ NI solution. 0.005 m. and 2 mm., 0.001 m. and 10 mm.

FIG. 24. Photometer record of $(C_5H_{11})_4$ NI solution. 0.005 m. and 2 mm., 0.0001 m. and 100 mm.

MAGNETIC SUSCEPTIBILITIES OF SOME ORGANIC COMPOUNDS IN DIFFERENT PHYSICAL STATES.

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1. *Introduction.*

Van Vleck[1] has shown that molecular susceptibility of a polyatomic molecule without a resultant spin can be represented as the sum of two terms.

$$\chi_m = -\frac{Le^2}{6mc^2}\Sigma\,\overline{r^2} + \tfrac{2}{3}L\,\Sigma\frac{|\,m_0\,(n':n)\,|^2}{h\nu\,(n':n)}$$

The first term is the well-known Langevin term and the second is a paramagnetic term independent of temperature, arising from the distorsion of the electron system due to the interatomic forces in the molecule. This paramagnetic term will vary with the state of the molecule. The magnitude of this term in the solid state, for example, will be different from the corresponding value in solution. When a salt is dissolved in a liquid, the binding forces in the solid state are destroyed, and the ions of the salt are surrounded by neighbouring solvent molecules which will also introduce some constraints.[2] In general therefore, we should expect a change in magnetic susceptibility when a salt is dissolved in solution (equal to the difference of the paramagnetic term in the two states). Several inorganic salts have been investigated by various workers and small changes of susceptibility observed in solution (on the average, about 2 to 3% increase in solution).[3]

No such work seems to have been undertaken in the case of organic compounds. Oxley[4] has shown that several aromatic compounds suffer a change (roughly 5% in most cases) in diamagnetic susceptibility on melting. In most cases there was an increase in value; but in a few cases a decrease was also observed. Whatever might be the sign of the change, it is clear that this must be due to some fundamental change taking place in the transition from the solid to the liquid phase. In the case of solutions of these organic compounds also, we should expect such a change in susceptibility.

In the present investigation, the susceptibilities of two important organic compounds, benzophenone and paranitrotoluene are studied in

the dissolved state, the solvent chosen being methyl alcohol. There are special reasons for choosing them for this investigation. If the substances studied by Oxley be examined, it will be found that most of them are liquids at room temperatures. But benzophenone and paranitrotoluene exist as solids at room temperatures and their melting points are not far removed from the ordinary temperatures. The melting point of benzophenone is 48° C. and that of paranitrotoluene 54° C. Hence these substances can be studied in the solid, dissolved and liquid (molten) states conveniently. Again they show opposite behaviour on melting; benzophenone shows an increase in susceptibility value on fusion while paranitrotoluene shows a decrease.

Oxley records an increase of 6% on fusion in the case of benzophenone. Krishnan, Guha and Banerjee,[5] on the other hand, find a change of only $2\frac{1}{2}$%. The latter authors interpret the large changes observed by Oxley as due to the effects of preferential orientation of microcrystals of the solid in the magnetic field. It appears doubtful whether this will completely explain Oxley's results. To investigate the problem at some length, experiment was undertaken to study the change of susceptibility on melting in the case of these two compounds.

Cabrera and Fahlenbrach[6] have also recently studied the changes during melting in the case of some organic compounds including paranitrotoluene. They record a decrease of about 4.3% for this compound on melting.

Incidentally, in the case of benzophenone a study of the supercooled state was made possible by the fact that benzophenone remains in the liquid condition even when it is cooled to room temperature. This is of special interest since the susceptibility value in the supercooled state was found to be slightly higher than that for the solid state.

2. *Experiment.*

The investigations were carried out with a Curie balance, the retorsion method being employed to take the deflections. Water was chosen as the standard, and its susceptibility was assumed to be 0.72.* The measurements were thoroughly standardised and the error does not exceed $\frac{1}{2}$%.

Benzophenone and paranitrotoluene of superior quality crystallised from pure methyl alcohol, were used in the experiments. Small thin bulbs which could be stoppered tightly were used for filling up the solutions and finding the deflections. After taking the deflections, the bulbs were kept open and the solution allowed to evaporate and deposit crystals. The

* All susceptibility values in this paper are to be multiplied by 10^{-6}.

bulbs were then weighed and thus the concentrations of the solutions were determined.

3. Results.

The susceptibility values of benzophenone, paranitrotoluene and methyl alcohol are given below along with those of other investigators.

TABLE I.

Substance	Author χ	Krishnan, Guha and Banerjee χ	Cabrera and Fahlenbrach χ	Kido[7] χ	Int.[8] Crit. Tables χ
Benzophenone ..	0·600	0·594	..	..	0·594
Paranitrotoluene	0·518	..	0·538	..	..
Methyl alcohol ..	0·685	..	0·674*	0·696	..

* *Zeit. f. Phys.*, 1933, **85**, 568.

The values obtained in this investigation are found to agree very satisfactorily with those of other investigators.

I. *Change in Solution.* (*a*) *Benzophenone.*—The results for the solution of benzophenone in methyl alcohol are given in Table II.

TABLE II.

Expt. No.	Weight of solution gr.	Wt. of benzophenone dissolved gr.	Concentration per cent.	Solution χ	Cal. χ	$\chi_{Sol.} - \chi_{Cal.}$	Difference for 100%
1	0·0489	0·0114	23·3	0·670	0·665	+0·005	+0·022
2	0·0819	0·0215	26·2	0·668	0·663	+0·005	+0·020
3	0·0664	0·0368	55·4	0·644	0·638	+0·006	+0·011
4	0·0924	0·0545	59·0	0·638	0·633	+0·005	+0·009
5	0·0733	0·0501	68·3	0·639	0·627	+0·012	+0·018
6	0·0818	0·0651	79·6	0·630	0·618	+0·012	+0·015

The sixth column gives the value of susceptibility calculated on the basis of the additive law and the seventh gives the difference. The last column gives difference in susceptibility value of benzophenone in solution and in the solid state.

On looking at the table, it is seen that there is a definite departure from the additive law. A large number of observations were taken of which six typical values are given above.

The average value of the last column (the difference between the susceptibility values of benzophenone in solution and in solid) works to 0.016. Hence the change in susceptibility in solution is $+ 0.016$. Its susceptibility in solution is therefore $0{\cdot}600 + 0.016 = 0.616 \pm 0.006$.

(*b*) *Paranitrotoluene.*—The results for paranitrotoluene-methyl alcohol solutions are given in Table III.

TABLE III.

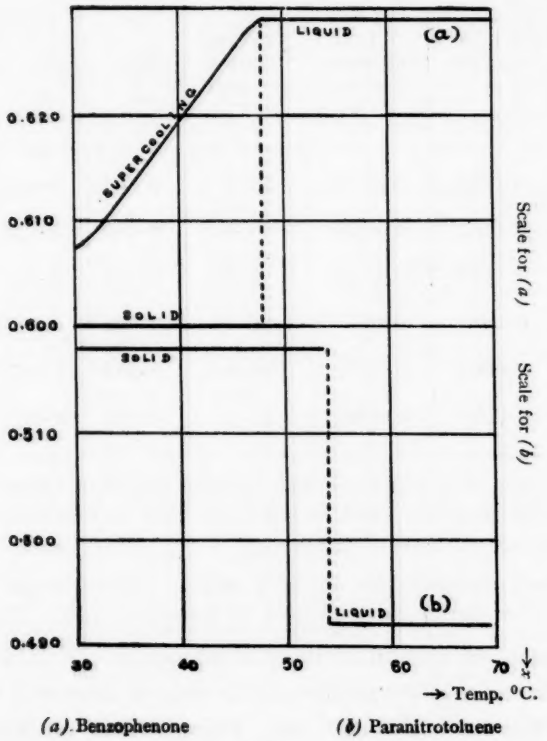
Concentration Number	Wt. of solution gr.	Wt. of substance dissolved gr.	Concentration per cent.	Soln. χ	Cal. χ	$\chi_{Sol.} - \chi_{Cal.}$
1	0·0808	0·0179	20·2	0·641	0·648	−0·007
2	0·0611	0·0130	21·3	0·640	0·650	−0·010
3	0·0702	0·0172	24·2	0·630	0·645	−0·015
4	0·0686	0·0197	28·7	0·628	0·637	−0·009
5	0·0605	0·0174	28·8	0·632	0·637	−0·005
6	0·0631	0·0200	31·7	0·624	0·632	−0·008

In this case, it is observed that the susceptibility value of paranitrotoluene in the dissolved state is less than that in the solid state. The average value of the last column ($\chi_{Soln.} - \chi_{Cal.}$) is found to be 0.009 and since the concentrations are only within a short range of 20 to 32% we may take the mean concentration to be nearly 26%. Hence the total change in value for paranitrotoluene in solution is $\frac{\cdot 009}{26} \times 100$; that is, $0.035 \pm .005$ and the susceptibility of the solid in solution is $0.483 \pm .005$.

II. *Change on Melting.* (*a*) *Benzophenone.*—Benzophenone was taken in a sealed bulb and suspended in the magnetic field inside a heater.

An initial reading was taken at room temperature and a small current was sent through the heater. The deflections were noted as the temperature gradually increased. Up to 48° C., the melting point of benzophenone, no change was observed. At 48° C. there was an increase in deflection (equivalent to 4.8%). Afterwards it remained constant up to 120° C. the maximum temperature reached in this experiment.

It was very interesting to study the changes during the process of cooling. With the gradual cooling of the substance below 48° C., a gradual decrease as distinct from a sudden decrease in value in passing through the melting point observed before, was noted. At room temperature (30° C.) the value of the supercooled liquid was definitely higher than the value in the solid state by 1.2%. The bulb was taken out and shaken to solidify the substance and it was found to have regained the original deflection for the solid state. These changes are shown by means of a graph. (See Fig. 1.)



(a) Benzophenone (b) Paranitrotoluene

FIG. 1.

(*b*) *Paranitrotoluene.*—Here a decrease of 5.1% was observed at the melting point (54° C.). The susceptibility remained constant up to and above the melting point. No such under-cooling effect as obtained in the case of benzophenone was observed. The substance began to crystallise as soon as the temperature fell below the melting point. The changes are shown by a graph. The results are given in Table IV.

TABLE IV.

Substance	Solid χ	Liquid χ	Change %
Benzophenone ..	0·600	0·629	+4·8
Paranitrotoluene ..	0·518	0·492	−5·1

Cabrera and Fahlenbrach noted a change of 4.3% in the case of paranitrotoluene. They have studied undercooling in the case of ortho- and paracresols. But they do not obtain such gradual decrease as observed here in the case of benzophenone. The susceptibility remains constant and equal to the value for the fused state in both cases.

4. Discussion.

Benzophenone and paranitrotoluene, the two substances investigated here, show the same order of susceptibility changes in solution as on melting. There is every reason to believe that other substances whose susceptibility alters on melting would similarly show a change in solution provided the proper solvents are chosen.

In a recent paper, Varadachari[9] has advanced the view that in a solid, there are polymers present which partially or completely decompose on melting. It is well known that a polymer, as distinguished from an associated complex, has got a definite structure and hence when a polymer decomposes there is a disruption of its structure as a consequence of which, there will be a change in susceptibility. Hence those solids which show a change in susceptibility on melting may be assumed to contain polymers which decompose on fusion. If a substance shows a temperature variation in susceptibility in the liquid state it is likely that the depolymerisation is only partial on melting and that the depolymerisation continues even above the melting point. As the temperature of the liquid is raised, the depolymerisation becomes complete at a specific temperature when no more polymers are present. The susceptibility will remain constant above that temperature. This has been observed by Cabrera and Fahlenbrach[10] in the

case of water which is known to contain various polymers in different proportions depending on the temperature. The susceptibility slightly increases with temperature and attains a constant value above 120° C. showing that above that temperature, water exists as simple molecules.

A similar theory can be extended to the state of solution, since we also observed a change in the susceptibility of the dissolved substance in such cases. However, the case of solutions is not so simple as that of melting. Solutions are complicated by the fact that the solute molecules (or the ions into which they may get dissociated) are surrounded by the molecules of the solvent which may introduce new linkages. In such a case, the change in susceptibility that we observe will depend on the medium in which the substance is dissolved. But in solutions which we have investigated, such conditions may not exist and the theory of decomposition of polymers will sufficiently explain the results.

It may be mentioned here that a study of the Raman effect of these substances in various physical states will give important and interesting results. Much information does not seem to be available in this direction. Raman effect data, coupled with the results of magnetic investigations, are bound to throw more light on the nature of solutions.

It is observed here that a change of about 5% in susceptibility value occurs in the case of benzophenone during melting. This agrees with that observed by Oxley. Krishnan, Guha and Banerjee, on the other hand, find a change of only 2.5%. These authors deduce the mean susceptibility of the substance from the three principal susceptibilities of the single crystal and compare this with the susceptibility value of the molten substance obtained by employing a different method.

These authors explain this discrepancy by suggesting that the orientations of the micro-crystals of the substance cannot be at random on account of the strong anisotropy of the crystal when the solids are obtained by cooling the liquid in a magnetic field. Goetz[11] who has made a special study of metallic crystals, has studied the effect of magnetic field on the growth of single crystals of bismuth. He found that crystals grown without a pre-determined orientation indicated a preference for an orientation in which the direction of the smallest diamagnetic susceptibility was parallel to the lines of force. He used a field of 20,000 gauss and he observed that this effect was much smaller than the orienting forces of a seed-crystal. It only proves the existence of micro-crystals even slightly above the melting point. The field that we ordinarily employ is even considerably less than 20,000 gauss (the author has worked with a magnetic field of 5,000 gauss) and hence the orientation effect due to the field in these cases must be very

small and probably even negligible. It is difficult to believe therefore whether the large change observed by Oxley and others can be explained by this effect. The change therefore appears to be genuine.

Cabrera and Fahlenbrach[9] have tried to find a relation between the change of susceptibility at the melting point and the dipole moment of the substance concerned. They plot a graph between ($\chi_{\text{liquid}} - \chi_{\text{solid}}$) and the dipole moment and draw a smooth curve passing evenly through the plotted points. The evidence however is not convincing. The points plot themselves at random. Besides, they have not studied substances of very high dipole moments which should show large changes on melting according to their theory. Further the force due to the dipole moment is only a body force and does not affect the electron system as has been proved in the case of liquid mixtures.[12] It is therefore difficult to suggest a definite relation between dipole moment and change in susceptibility on fusion. The explanation on the basis of break-up of polymers seems to be nearest the truth.

Summary.

Benzophenone and paranitrotoluene have been studied in the solid and fused states. Their solutions in methyl alcohol have also been investigated and the changes of susceptibility on dissolving solution are found to be in the same direction as those on melting. The supercooled state in the case of benzophenone has also been examined. The experiments lend support to the theory that the changes on melting and solution could be attributed to the break-up of polymers present in the solid state.

I take this opportunity of thanking Dr. S. Ramachandra Rao for his interest and guidance. My thanks are also due to the authorities of the Annamalai University for the award of a studentship.

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MAGNETIC STUDIES OF SULPHUR AND SOME SULPHUR COMPOUNDS.

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1. Introduction.

It is well known that sulphur exists in various complexes. X-ray analysis[1] in rhombic crystals shows that the molecule of sulphur in the crystal exists as S_{16}. The nature of sulphur complexes has also been investigated in various solutions by studying their vapour pressures and molecular weights.[2] One of the objects of the present investigation is to determine the state of sulphur in solutions purely by magnetic method.

Krishnamurti[3] studied the Raman spectrum of rhombic sulphur in the form of small crystals. On dissolving sulphur in carbon disulphide he found that one of the lines attributed to the S_{16} molecule disappeared. He also records three strong lines as present both in solid and in solution and attributes them to S_8 molecules. We have chosen carbon disulphide and sulphur monochloride as the solvents since sulphur has a high solubility in these liquids (about 55% and 65% respectively at room temperature). The evidence from vapour pressure measurements on the state of sulphur in solutions of sulphur monochloride is not conclusive. Some measurements point to the existence of S_2 in the solution while others indicate the presence of S_8 molecules.[4] A study of this solution was therefore undertaken with a view to throw some light on this question.

Compounds of sulphur also present an interesting study, because of the different valencies exhibited by the element in chemical combination. Pascal[5] was the first to study the magnetic susceptibilities of several sulphur compounds. More recently a few compounds of sulphur were studied by Farquharson[6] with the Curie-Cheneveau balance. Kido[7] also investigated a number of sulphur compounds and derived susceptibility values for several incomplete ions of sulphur. His study also included a number of homopolar compounds from which he established the applicability of the additive law to such compounds.

Varadachari[8] studied the diamagnetic susceptibilities of crystalline sulphates of lithium, sodium, potassium and magnesium. His results show that the nature of the bond between the water molecules and the sulphate ion is a loose one. Sodium and potassium sulphides were also investigated by him. A graph drawn between the susceptibility of different incomplete sulphur ions and the valency of sulphur gave a straight line thus confirming Kido's result.

We have studied the mono- and di-chlorides of sulphur, thionyl and sulphuryl chlorides and sulphur iodide and the results we have obtained are of special interest from the point of view of their molecular structure.

2. *Experiment.*

Susceptibility measurements were made with a Curie balance, the retorsion method being employed to bring the specimens in the identical position with the field on. Water was chosen as the standard substance, its susceptibility being taken as 0·72.* The substances were contained in thin glass bulbs provided with air-tight stoppers. The bulbs were weighed before and after the deflections were taken to detect losses by evaporation in the case of liquids.

Sulphur crystals were purified by crystallising from solutions in pure distilled carbon disulphide. The substances used were of the purest quality obtained from Kahlbaum or Merck. An average deflection of about 20 cm. was obtained in most cases. The deflection of the standard bulbs was taken before and after each experiment to correct for any errors that may arise from fluctuations in the constants of the apparatus.

Solutions of sulphur in carbon disulphide were studied for various concentrations. The bulbs were filled with the solutions, stoppered tightly, weighed and suspended from the Curie balance. After noting the deflection the bulbs were left open for a time to allow the liquid to evaporate away, and the deposited sulphur weighed. The concentrations of the solutions were thus determined.

In the case of sulphur solutions in its monochloride, the determination of the concentrations is not so easy, since sulphur monochloride hydrolyses on exposure to air and leaves sulphur behind. We have taken weighed quantities of the solute and the solvent and believe that the concentrations of the solutions investigated should have been between 50 and 60%.

3. *Results.*

(*a*) *Sulphur in carbon disulphide.*—The diamagnetic susceptibility of carbon disulphide was found to be 0·556. This agrees very closely with the

* In this paper all the susceptibility values must be multiplied by 10^{-6}.

value of 0·54 given in the *International Critical Tables;* as well as 0·565 of one of us,[8] and 0·550 of Rao and Sivaramakrishnan.[9] For sulphur we obtained 0·457. We may mention that this is slightly less than 0·485 obtained by Owen,[10] 0·487 by Bhatnagar and Mathur[11] and 0·481 by one of us.[8]

The results obtained with solutions of sulphur in carbon disulphide having concentrations varying from about 12 to 56% are given below. The calculated values of the diamagnetic susceptibility of the solutions based on the assumption of the additive law are given in the sixth column. In the last column the difference between the observed and calculated values are shown.

Concentration No.	Weight of solution	Weight of sulphur dissolved	Concentration per cent.	Solution χ	Calculated χ	$\chi_{Solution} - \chi_{Calculated}$
	Gm.	Gm.				
1	0·0974	0·0117	12·0	0·546	0·544	+0·002
2	0·0666	0·0134	20·1	0·540	0·536	+0·004
3	0·0661	0·0146	22·1	0·532	0·534	−0·002
4	0·0662	0·0160	24·2	0·538	0·532	+0·006
5	0·0978	0·0292	29·9	0·529	0·526	+0·003
6	0·1032	0·0334	32·4	0·529	0·524	+0·005
7	0·0984	0·0342	34·8	0·526	0·521	+0·005
8	0·0709	0·0250	35·3	0·524	0·521	+0·003
9	0·0895	0·0359	40·1	0·520	0·516	+0·004
10	0·0717	0·0297	41·4	0·520	0·515	+0·005
11	0·0900	0·0390	43·4	0·521	0·513	+0·008
12	0·1041	0·0455	43·7	0·513	0·513	+0·000
13	0·1223	0·0535	43·7	0·520	0·513	+0·007
14	0·0763	0·0414	54·3	0·509	0·502	+0·007
15	0·1526	0·0858	56·2	0·506	0·500	+0·006

It will be noted that the difference in the last column is in most cases within the limits of error. But sometimes the deviation works to as much as 1.5% from which it appears to follow that small alterations in the diamagnetic susceptibility accompany the breaking down of the S_{16} complex into lower complexes in solution. A more careful scrutiny of the results suggests that such a deviation may be genuine; for, if there be a change of about 1% in solution, the deviations in the last column would tend to lie between $\frac{1}{2}$ and $1\frac{1}{2}$ per cent., on the assumption that the error in our results is $\frac{1}{2}$%. In most cases, this is just what is found. We may therefore conclude that the breaking down of the S_{16} complex is accompanied by an increase in the diamagnetic susceptibility. Such an increase has a theoretical background in the fact that the Van Vleck[12] paramagnetic term would show a decrease in value when the complex breaks down.

(*b*) *Sulphur in sulphur monochloride.*—Sulphur monochloride appeared yellowish red and fumed in air. The average diamagnetic susceptibility of the liquid was found to be 0.461. We have not been able to find any previous measurements for this liquid.

As mentioned earlier in this paper, concentrated solutions of sulphur in its monochloride were prepared and investigated. The results obtained with half a dozen solutions are given below.

Experiment number	Weight of solution Gr.	Solution χ
1	0·1099	0·462
2	0·1090	0·458
3	0·1075	0·458
4	0·1020	0·461
5	0·0672	0·458
6	0·1322	0·462

The value of the susceptibility of the solution remains the same as that of sulphur (0.457) and sulphur monochloride (0.461). Orndorff and Terrasse[13] suggest from their investigations based on boiling point determinations that sulphur exists as S_2 in sulphur monochloride. It is well known that S_2 like O_2 is paramagnetic. Our results do not indicate any deviation in the susceptibility and hence it may be concluded that no S_2 molecules are formed when sulphur is dissolved in its monochloride.

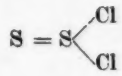
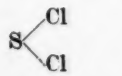
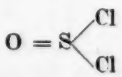
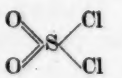
The solutions contained in small bulbs were heated to temperatures up to about 120° C. and the susceptibilities at different temperatures determined. No change in the susceptibility was observed indicating that the elevation of temperature does not favour the production of S_2 complex.

(*c*) *Compounds of sulphur.*—The following compounds have been studied; sulphur monochloride, sulphur dichloride, thionyl chloride, sulphuryl chloride and sulphur iodide. The results are shown in the accompanying table. In column 2 are shown the structural formulæ supported by magnetic evidence. The calculated values of the molecular susceptibility given in the last column have been calculated from the ionic values given by Kido.

Kido's Values.

Ion	Molecular susceptibility
S^{-2}	27.4
S^{0}	(14.6)*
S^{+2}	5.2
S^{+4}	−4.6
S^{+6}	−15.0
Cl^{-1}	22.1
O^{-2}	13.7
I^{0}	44.4†

* The value is ours. † Value taken from *Int. Crt. Tables.*

Compound	Structure	Diamagnetic mass susceptibility	Diamagnetic Molecular susceptibility	
			Observed	Calculated
S_2Cl_2		0·461	62·2	67·0
SCl_2		0·467	48·1	49·4
$SOCl_2$		0·372	44·3	53·3
SO_2Cl_2		0·365	49·3	56·6
SI	S + I	0·329	52·7	54·0

It will be seen that in the second case, the calculated and observed values nearly agree. However, the difference is somewhat greater in the case of the monochloride. This may be attributed to the stronger binding between the two sulphur atoms.

Such a striking difference exists also in the case of thionyl chloride. This departure may again be due to a strong binding between the sulphur and oxygen atoms, which introduces ionic deformation and consequently a high paramagnetic term in the total molecular susceptibility. The diamagnetic susceptibility of the compound is thus reduced and the magnitude of the difference between the observed and calculated values may be taken as a measure of the strength of binding between the atoms in the molecule.

The case of sulphuryl chloride is of special interest since sulphur in this molecule has been considered as tetravalent by some chemists and hexavalent by others. The magnetic data support the latter view. For, if sulphur was tetravalent its molecular susceptibility would work to 67.0 as against 56.6 shown in our tables.

Considerable evidence on chemical grounds has been advanced in support of the view that all the so-called sulphur iodides are only mixtures of sulphur and iodine.[14] Our results also support this view. If sulphur iodide is a compound with the molecular structure $S{=}S\begin{matrix}I\\I\end{matrix}$ then the molecular susceptibility of SI would work to 64.6 as against the observed value of 52.7. On the other hand, assuming SI to be a mixture, the molecular susceptibility is calculated to be 54.0 which agrees closely with the observed value. Some investigators have suggested that the substance has the characters of metal alloys and that the mono-iodide is in a feeble state of combination. These conclusions are entirely supported by our results.

4. Summary.

Solutions of sulphur in carbon disulphide and sulphur monochloride have been studied by the Curie method. Small deviations of the order of 1 per cent. have been observed for solutions in carbon disulphide. This has been attributed to the breaking down of S_{16} molecule. No evidence has been obtained to indicate the presence of S_2 in sulphur monochloride solutions. A few halides of sulphur have also been investigated. The results throw useful light on the valency of sulphur in the different compounds.

We take this opportunity of thanking the authorities of the Annamalai University for the award of studentships which enabled us to undertake this investigation. Our thanks are also due to Dr. S. Ramachandra Rao for his interest in this work.

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VORTEX MOTION IN RECTANGULAR CYLINDERS.

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The general problem of the motion of a liquid due to a rectilinear vortex in a cylinder whose cross-section is bounded by four arcs of mutually orthogonal curves can be readily solved with the help of conformal transformation. By considering the infinite series of images in the four bounding planes Greenhill[1] has solved two particular cases. From his analysis it appears that this method of images is bound to be rather long and inconvenient in the general case. Moreover it is not always free from preliminary limitations which may not be found essential when the solution of the problem has been obtained. For example, in the case of a rectangle bounded by two concentric arcs and two radii inclined at an angle $\frac{1}{n}\pi$ Greenhill has to make the supposition in the beginning that $\frac{1}{n}\pi$ is a sub-multiple of two right angles. As he remarks at the end of his paper his solution holds good whatever $\frac{1}{n}\pi$ may be.[2]

We take the plane of a cross-section as the plane of a complex variable z. Let a system of orthogonal curves in the z-plane be given by

$$\omega = \alpha + i\beta = f(z);$$

so that the sides of the z-rectangle can be taken as $\alpha = 0$, $\alpha = 2K$, $\beta = 0$, and $\beta = 2K'$, K and K′ being two constants. The ω-rectangle can be mapped on a ζ-half plane by means of the relation

$$\omega = A\int[(\zeta-\xi_1)(\zeta-\xi_2)(\zeta-\xi_3)(\zeta-\xi_4)]^{-\frac{1}{2}}\,d\zeta + B, \qquad .. \quad (1)$$

ξ_1, ξ_2, ξ_3, and ξ_4 being the points on the real axis in the ζ-plane that correspond to the angular points P, Q, R, and O in the ω-plane.

Putting $\xi_1 = k'/k$, $\xi_2 = \infty$, $\xi_3 = -k/k'$, and $\xi_4 = 0$, we get

$$\omega = A\int[\zeta(\zeta + k/k')(\zeta - k'/k)]^{-\frac{1}{2}}\,d\zeta + B.$$

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1 Greenhill, *Quart. J. of Math.*, 1877, 15, 23-29.

2 This limitation in the method of images has been pointed out by Ramsey in his *Hydromechanics*, Part 2, Art. 189, (1913) edition.

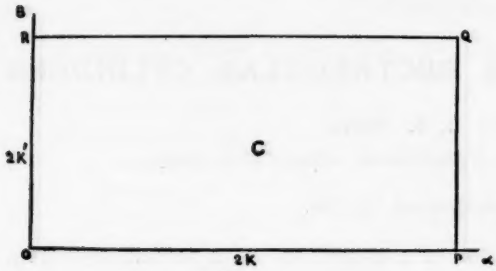

FIG. 1.

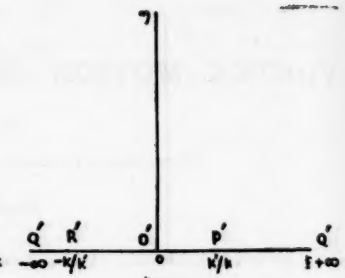

FIG. 2.

Adjusting the constants A and B we can write[3]

$$\zeta = -\,k/k'\,\mathrm{Cn}^2(\tfrac{1}{2}\,\omega - \mathrm{K} - i\mathrm{K}') = k'/k\,nc^2\,(\tfrac{1}{2}\omega) \quad .. \quad .. \quad (2\cdot1)$$

$$= \frac{k}{k'}\,\frac{dn\,\omega - \mathrm{Cn}\,\omega}{1 - dn\,\omega}, \quad .. \quad .. \quad .. \quad .. \quad (2\cdot2)$$

k being the modulus, and $4\mathrm{K}$, $4i\mathrm{K}'$ the periods of the elliptic function. Referred to C, the centre of the ω-figure, as the origin this transformation becomes

$$\zeta = \frac{i\,(1 + k\,\mathrm{Sn}\,\omega)}{\mathrm{Cn}\,\omega - i\,k'\,\mathrm{Sn}\,\omega} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2\cdot3)$$

Hence the relation

$$\zeta = \frac{i\,[1 + k\,\mathrm{Sn}\,\{f\,(z)\}]}{\mathrm{Cn}\,\{f\,(z)\} - i\,k'\,\mathrm{Sn}\,\{f\,(z)\}} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

transforms the z-rectangle into the upper half of the ζ-plane.

Let there be a vortex of strength m at a point z_0 within the z-rectangle, and let ω_0 and ζ_0 be the corresponding points of the ω-plane and ζ-plane. If ϕ is the velocity potential and ψ the stream function of the motion, we know that

$$\phi + i\,\psi = \frac{mi}{2\pi}\log\frac{\zeta - \zeta_0}{\zeta - \zeta_0'}, \quad .. \quad .. \quad .. \quad .. \quad (4)$$

which, after using (2.1), becomes

$$\phi + i\,\psi = \frac{mi}{2\pi}\log\frac{\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z_0')\}\,[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z)\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z_0)\}]}{\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z_0)\}\,[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z)\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z_0')\}]}, \quad (5)$$

where $\zeta_0' = \xi_0 - i\,\eta_0$ and $z_0' = x_0 - iy_0$. The stream function is, therefore, given by

$$\psi = \frac{m}{4\pi}\log\frac{[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z)\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z_0)\}]\,[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z')\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z_0')\}]}{[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z)\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z_0')\}]\,[\mathrm{Cn}^2\,\tfrac{1}{2}\,\{f\,(z')\} - \mathrm{Cn}^2\,\tfrac{1}{2}\,\{f(z_0)\}]} \quad .. \quad (6)$$

[3] We have followed Dr. Glaisher in writing $ncu = 1/cnu$, with a similar notation for the other elliptic functions.

To determine the curve described by the vortex we apply the well-known result due to Routh,[4] *viz.*

$$\chi(x, y) = \chi(\xi, \eta) + \frac{m}{4\pi} \log \left| \frac{d\zeta}{dz} \right|, \qquad \ldots \quad (7)$$

$\chi(x, y)$ being the stream function for the motion of the vortex in the z-plane and $\chi(\xi, \eta)$ of the corresponding vortex in the ζ-plane. From (4) we easily get

$$\chi(\xi, \eta) = -\frac{m}{4\pi} \log \eta. \qquad \ldots \quad (8)$$

η and $|\, d\zeta/dz \,|$ can be determined either from (2.2) or from (3) according as O or C in Fig. 1 is taken as the origin. Taking (2. 2) we have

$$2i\eta = \frac{k}{k'}\left[\frac{dn\,\omega - \mathrm{Cn}\,\omega}{1 - dn\,\omega} - \frac{dn\,\omega' - \mathrm{Cn}\,\omega'}{1 - dn\,\omega'}\right]$$

$$= \frac{k}{k'}\left[\frac{(dn\,\omega - dn\,\omega') - (\mathrm{Cn}\,\omega - \mathrm{Cn}\,\omega') + (\mathrm{Cn}\,\omega\, dn\,\omega' - \mathrm{Cn}\,\omega'\, dn\,\omega)}{(1 - dn\,\omega)(1 - dn\,\omega')}\right],$$

which, after using Jacob's addition formulæ[5] for the various terms in square brackets, becomes

$$2i\eta = -\frac{k}{k'} \frac{\mathrm{Sn}\,a\,\mathrm{Sn}\,i\beta\,(k'^2 + k^2\,\mathrm{Cn}\,a\,\mathrm{Cn}\,i\beta - dn\,a\,dn\,i\beta)}{(dn\,a - dn\,i\beta)^2}$$

$$= -\frac{k}{k'} \frac{\mathrm{Sn}\,a\,\mathrm{Sn}\,i\beta}{\mathrm{Cn}\,a + \mathrm{Cn}\,i\beta} \cdot \frac{dn\,a\,\mathrm{Cn}\,i\beta - dn\,i\beta\,\mathrm{Cn}\,a}{dn\,a - dn\,i\beta} \qquad \ldots \quad (9)$$

Again we have

$$\left|\frac{d\zeta}{dz}\right|^2 = \left|\frac{d\zeta}{d\omega} \cdot \frac{d\omega}{dz}\right|^2 = \left|\frac{d\zeta}{d\omega}\right|^2 f'(z)\, f'(z'),$$

where $f'(z) = d\{f(z)\}/dz$. Using (2·1) we get

$$\left|\frac{d\zeta}{d\omega}\right|^2 = \frac{k'^2}{k^2} \cdot \frac{\mathrm{Sn}\,\tfrac{1}{2}\omega\,\mathrm{Sn}\,\tfrac{1}{2}\omega'\,dn\,\tfrac{1}{2}\omega\,dn\,\tfrac{1}{2}\omega'}{\mathrm{Cn}^3\,\tfrac{1}{2}\omega\,\mathrm{Cn}^3\,\tfrac{1}{2}\omega'}.$$

Since[6]

$$\mathrm{Sn}\,\tfrac{1}{2}\omega\,\mathrm{Sn}\,\tfrac{1}{2}\omega' = \frac{1}{k^2} \cdot \frac{dn\,i\beta - dn\,a}{\mathrm{Cn}\,i\beta - \mathrm{Cn}\,a},$$

$$\mathrm{Cn}\,\tfrac{1}{2}\omega\,\mathrm{Cn}\,\tfrac{1}{2}\omega' = \frac{k'^2}{k^2} \cdot \frac{dn\,i\beta - dn\,a}{\mathrm{Cn}\,i\beta\,dn\,a - \mathrm{Cn}\,a\,dn\,i\beta},$$

$$dn\,\tfrac{1}{2}\omega\,dn\,\tfrac{1}{2}\omega' = k'^2 \frac{cn\,i\beta - cn\,a}{cn\,i\beta\,dn\,a - cn\,a\,dn\,i\beta},$$

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[4] Routh, *Proc. London Math. Soc.*, 1881, **12**, 82-84; also Ramsey *Hydromechanics*, Part 2, pp. 224-5 (1913 edition).

[5] See Cayley, *Elliptic Functions*, 1876, 65-66.

[6] For these formula reference may be made to Greenhill, *Applications of Elliptic Functions*, (1892), 255.

we have

$$\left|\frac{d\zeta}{d\omega}\right|^2 = \frac{k^2}{k'^2}\cdot\frac{\mathrm{Cn}\,i\,\beta - \mathrm{Cn}\,\alpha}{\mathrm{Cn}\,i\,\beta + \mathrm{Cn}\,\alpha}\cdot\frac{(\mathrm{Cn}\,i\,\beta\,dn\,\alpha - \mathrm{Cn}\,\alpha\,dn\,i\,\beta)^2}{(dn\,\alpha - dn\,i\,\beta)^2}, \quad .. \quad (10)$$

and hence (7) and (8) give

$$\chi(x, y) = \frac{m}{8\pi}\log\frac{4(\mathrm{Cn}^2\alpha - \mathrm{Cn}^2\,i\,\beta)}{\mathrm{Sn}^2\,\alpha\,\mathrm{Sn}^2\,\beta}f'(z)\,f'(z')$$

$$= \frac{m}{8\pi}\log 4\,(n\mathrm{S}^2\,\alpha - n\mathrm{S}^2\,i\,\beta)\,f'(z)\,f'(z')$$

$$= \frac{m}{8\pi}\log 4\,[n\mathrm{S}^2(\alpha, k) + n\mathrm{S}^2(\beta, k') - 1]\,f'(z)\,f'(z') \quad .. \quad (11)$$

If we put

$$\omega = \alpha + i\,\beta = f(z) = f_1(x, y) + i\,f_2(x, y),$$

we get

$$\chi(x, y) = \frac{m}{8\pi}\log 4\,[n\mathrm{S}^2\{f_1(x, y), k\} + n\mathrm{S}^2\{f_2(x, y), k'\} - 1]$$

$$\times f'(z)\,f'(z'); \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

so that the curve described by the vortex is given by

$$[n\mathrm{S}^2\{f_1(x, y), k\} + n\mathrm{S}^2\{f_2(x, y), k'\} - 1]\,f'(z)\,f'(z') = \text{a constant.} \quad (13)$$

When the rectangle in the z-plane is rectilinear we have $\omega = z$, and the stream lines are given from (6) as

$$\frac{(cn^2\,\frac{1}{2}\,z - cn^2\,\frac{1}{2}\,z_0)\,(cn^2\,\frac{1}{2}\,z' - cn^2\,\frac{1}{2}\,z_0')}{(cn^2\,\frac{1}{2}\,z - cn^2\,\frac{1}{2}\,z_0')\,(cn^2\,\frac{1}{2}\,z' - cn^2\,\frac{1}{2}\,z_0)} = \text{constant.}$$

The curve described by the vortex is

$$ns^2(x, k) + ns^2(y, k') = \text{a constant}^7 \quad .. \quad .. \quad .. \quad (14)$$

Referred to the centre of the rectangle as origin it becomes

$$k'^2\,nc^2(x, k) + k^2\,nc^2(y, k') = \text{a constant} \quad .. \quad .. \quad .. \quad (15)$$

For a square cross-section we have

$$\mathrm{K} = \mathrm{K}' = 1{\cdot}854; \quad k = k' = 1/\sqrt{2},$$

and (15) reduces to

$$nc^2(x, k) + nc^2(y, k) = c \text{ (say)}.$$

In Fig. 3 I have traced some of these curves in the first quadrant by taking $c = 3, 4, 7, 31$. Obviously these curves are symmetrical both about the co-ordinate axes and the lines $x \pm y = 0$.

The vortex is stationary when at the centre of the rectangle. Using (3) and (4) and noticing that $\zeta = i$ corresponds to $z = 0$ we get

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[7] This result is the same as obtained by Greenhill, *loc. cit.*, 25.

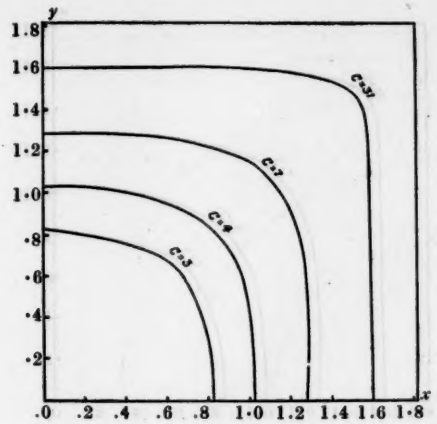

FIG. 3.

$$\phi + i\psi = \frac{mi}{2\pi} \log \frac{\zeta - i}{\zeta + i}$$

$$= \frac{mi}{2\pi} \log \frac{1 - \mathrm{Cn}\, z + (k + i\,k')\,\mathrm{Sn}\, z}{1 + \mathrm{Cn}\, z + (k - i\,k')\,\mathrm{Sn}\, z}$$

$$= \frac{mi}{2\pi} \log \frac{(k + i\,k')\,\mathrm{Sn}\, z}{1 + \mathrm{Cn}\, z} = \frac{mi}{4\pi} \log \frac{1 - \mathrm{Cn}\, z}{1 + \mathrm{Cn}\, z}, \quad .. \quad (16)$$

neglecting a constant.

The stream function[8] of the motion is given by

$$\psi = \frac{m}{8\pi} \log \frac{(1 - \mathrm{Cn}\, z)\,(1 - \mathrm{Cn}\, z')}{(1 + \mathrm{Cn}\, z)\,(1 + \mathrm{Cn}\, z')}$$

$$= \frac{m}{4\pi} \log \frac{\mathrm{Cn}\, x - \mathrm{Cn}\, i\, y}{\mathrm{Cn}\, x + \mathrm{Cn}\, i\, y} = \frac{m}{2\pi} \tanh^{-1} \frac{\mathrm{Cn}\, x}{\mathrm{Cn}\, i\, y}$$

$$= \frac{m}{2\pi} \tanh^{-1} \{\mathrm{Cn}\,(x, k)\ \mathrm{Cn}\,(y, k')\} \quad .. \quad .. \quad .. \quad (17{\cdot}1)$$

In like manner

$$\phi = -\frac{m}{2\pi} \tan^{-1} \frac{\mathrm{Sn}\,(x, k)\ dn\,(y, k')}{\mathrm{Sn}\,(y, k')\ dn\,(x, k)} \quad .. \quad .. \quad .. \quad (17{\cdot}2)$$

The equation of the stream lines is, therefore, given by

$$\mathrm{Cn}\,(x, k)\ \mathrm{Cn}\,(y, k') = \text{a constant} = c \text{ (say)} \quad .. \quad .. \quad (18)$$

By taking $c = \cdot1, \cdot25, \cdot5, \cdot75$, I have traced the corresponding stream lines in Fig. 4 for the first quadrant of a square cross-section.

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[8] Greenhill, *loc. cit.*, 26.

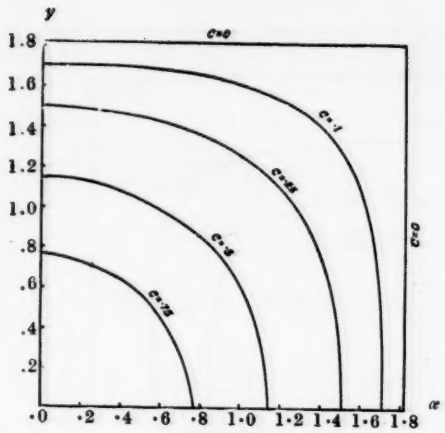

FIG. 4.

When the cross-section is bounded by two concentric arcs of radii a and b, and two radii inclined at an angle ϵ we have the relation

$$\omega = \alpha + i\beta = \frac{2K'}{\epsilon} \log \frac{z}{a} = \frac{2K'}{\epsilon}\left(\log \frac{r}{a} + i\theta\right) \quad .. \quad .. \quad (19)$$

where it is assumed that $\alpha = 0$, $\alpha = 2K$, $\beta = 0$, $\beta = 2K'$ correspond with $r = a$, $r = b$, $\theta = 0$, $\theta = \epsilon$ respectively. (6) and (13) give the stream function of the motion as

$$\psi = \frac{m}{4\pi} \log \frac{[Cn^2\{(K'/\epsilon)\log(z/a)\} - Cn^2\{K'/\epsilon)\log(z_0/a)\}]}{[Cn^2\{(K'/\epsilon)\log(z/a)\} - Cn^2\{K'/\epsilon)\log(z_0'/a)\}]} \times \frac{[Cn^2\{(K'/\epsilon)\log(z'/a)\} - Cn^2\{K'/\epsilon)\log(z_0'/a)\}]}{[Cn^2\{(K'/\epsilon)\log(z'/a)\} - Cn^2\{K'/\epsilon)\log(z_0/a)\}]} \quad .. \quad (20)$$

and the curve described by the vortex as

$$\frac{1}{r^2}\left[nS^2\left(\frac{2K'}{\epsilon}\log\frac{r}{a}, k\right) + nS^2\left(\frac{2K'\theta}{\epsilon}, k'\right) - 1\right] = \text{a constant} \quad .. \quad (21)$$

a result quite laboriously obtained by Greenhill.[9]

I do not think Greenhill is right when he says that the vortex is stationary when $r = \sqrt{ab}$, $\theta = \frac{1}{2}\epsilon$. This can be easily seen from (11) if we form the values of $\partial\chi/\partial x$ and $\partial\chi/\partial y$. What actually happens is that the corresponding vortex at the centre of the ω-rectangle is always stationary. The point $r = \sqrt{ab}$, $\theta = \frac{1}{2}\epsilon$, in the z-plane corresponds to the centre, C, in the ω-plane. Apparently Greenhill assumes that corresponding vortices in two conformally represented planes continue to move so as to occupy corresponding points. We easily see from (7) that in general this is not true.

[9] *Loc. cit.*, 28.

In the present case the point at which the vortex is stationary is readily found from the condition

$$\frac{\partial \chi}{\partial r} = 0, \frac{\partial \chi}{\partial \theta} = 0$$

Using (11) we get

$$\beta = \mathrm{K}', \textit{ i.e., } \theta = \tfrac{1}{2}\epsilon,$$

and

$$1 + \frac{2\mathrm{K}'}{\epsilon} \frac{Cn\ a\ dn\ a}{Sn\ a} = 0,$$

i.e.,

$$\frac{dn\ 2a + Cn\ 2a}{dn\ 2a - Cn\ 2a} = \frac{\epsilon^2}{4k'^2\ \mathrm{K}'^2},$$

or

$$Sn\ (2a - \mathrm{K}) = Sn\left(\frac{4\mathrm{K}'}{\epsilon} \log \frac{r}{a} - \mathrm{K}\right) = \frac{4k'^2\mathrm{K}'^2 - \epsilon^2}{4k'^2\mathrm{K}'^2 + \epsilon^2} \quad .. \quad (22)$$

which determines r. We also have the relation

$$\frac{\mathrm{K}}{\mathrm{K}'} = \frac{\log\ (b/a)}{\epsilon}$$

To take a simple example we put $\mathrm{K} = \mathrm{K}' = 1{\cdot}854$, $k = k' = 1/\sqrt{2}$, $a = 1$, $\epsilon = \frac{1}{2}\pi$. The value of b is $e^{\frac{1}{2}\pi} = 4{\cdot}810$. From (22) we get

$$Sn\left(\frac{8\mathrm{K}}{\pi} \log r - \mathrm{K}\right) = 0{\cdot}472,$$

i.e., $$\log r = \tfrac{1}{8}\pi\left(1 + \frac{0{\cdot}503}{\mathrm{K}}\right) = 0{\cdot}499$$

or $$r = 1{\cdot}647.$$

Thus the point at which the vortex is stationary is given by $r = 1{\cdot}647$, $\theta = \frac{1}{4}\pi$. According to Greenhill the value of r should be $\sqrt{b}$, *i.e.*, $2{\cdot}193$.

When the rectangle is formed by arcs of co-axial circles we can take

$$\omega + (\alpha_1 + i\,\beta_1) = -\,\mu \log \frac{z - a}{z + a} \quad .. \quad .. \quad .. \quad (23)$$

so that the ω-rectangle is given by $\alpha = 0$, $\alpha = \alpha_2 - \alpha_1 = 2\mathrm{K}$, $\beta = 0$, $\beta = \beta_2 - \beta_1 = 2\mathrm{K}'$. Putting $z - a = r_1\ e^{i\theta_1}$, $z + a = r_2\ e^{i\theta_2}$, we get from (11)

$$-\frac{1}{r_1^2\ r_2^2}\left[nS^2\left\{\left(\mu \log \frac{r_1}{r_2} + \alpha_1,\ k\right)\right\} + nS^2\left\{\mu\ (\theta_1 - \theta_2) + \beta_1,\ k'\right\} - 1\right] = \text{a constant} \quad .. \quad (24)$$

as the curve described by the vortex.

In like manner when the sides are arcs of confocal conics we can get the corresponding results by using the relation

$$\omega + (\alpha_1 + i\,\beta_1) = \sin^{-1}\frac{z}{c},$$

the ω-rectangle being the same as in the last example.

DIFFRACTION OF LIGHT BY ULTRASONIC WAVES.

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Part I. Effect of Oblique Incidence.

In a series of interesting papers, Sir C. V. Raman and N. S. Nagendra Nath[1] have developed a theory for the diffraction of light by high frequency sound waves, the essential idea being the diffraction of the corrugated form of the transmitted wave-front of light. Their theory has been able to explain many of the experimental results of R. Bär[2] and of Debye and Sears.[3] In Part II of their theory they have very satisfactorily explained the curious phenomenon of the wandering of the intensities of the various orders observed first by Debye and Sears on tilting the trough containing the liquid. Their theory also explains the disappearance of the diffraction effects at greater angles of obliquity. The standpoint developed by them in Parts IV and V of their series, based on the wave-equation governing the propagation of light in a medium filled with sound waves explains the asymmetry in the diffraction pattern. In this paper the author presents detailed results of investigation with regard to the asymmetry observed in the diffraction spectra.

The asymmetry in the diffraction spectra was observed, simultaneously and independently by Lucas and Biquard,[4] and by Debye and Sears in their earliest papers, and later by the author while carrying out determinations of ultrasonic velocities in various organic liquids. It has been recently investigated in detail by Bär[5] also.

Results.

The experimental arrangement was the one followed earlier and described in previous papers.

It was found by the author that when the quartz crystal, set up to excite vibrations in the liquid, is inclined to the incident parallel beam, then an asymmetry in the diffraction spectra was observed.

Fig. 1 shows the arrangement. θ represents the angle through which the quartz plate Q is turned in the direction shown by the arrow, and is

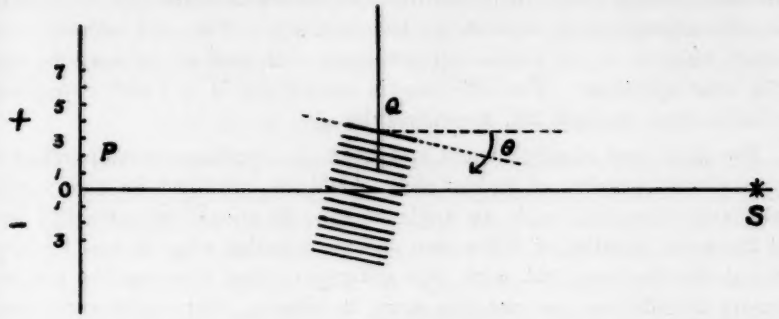

FIG. 1.

given in Fig. 2, in minutes of arc. P is the ground-glass plate on which are received the diffraction spectra. The upper portion is the right side (say +) where the greater number of orders is observed when the tilt is as shown in the diagram.

It is necessary to make exact determinations of the angle of inclination for obtaining the relationship between the nature of asymmetry in the spectra and the angle of inclination. This can be useful to test further the theory relating to the diffraction spectra.

To the centre of the ebonite piece carrying the quartz crystal, of 20 × 20 × 2 mms., a straight rigid steel rod of 310 mms. in length was firmly attached by sealing wax. The free-end of the rod, which was sharp and pointed, moved over a vertical scale, divided into millimeters, so that any small inclination could be read off accurately.

A series of photographs of the spectra were taken at different inclinations of the quartz, with the parallel position marked zero. The frequency employed was 7.37×10^6 c./s., while only the spectra for 5461 Å of the mercury arc were photographed.

We describe below, the positions, number and intensities of the different orders, as seen visually, at various angles of inclination. Fig. 2 bears this out amply. The intensities are not accurate but should be taken as indicative of the progress of changes accompanying the inclination.

The liquid, benzene, was contained in a tall vessel 12″ high with plane plates serving as walls. Progressive waves were employed throughout.

For incident light parallel to the sound wave-front, the position indicated by 0 in the figure (Fig. 2), the number of orders is equal on either side, with symmetrical distribution of intensity. At a small angle of even 6′, the fifth order on the right (say +) has begun to brighten up, almost double

in intensity, while it is evident that other orders on the same side are brighter than the corresponding ones on the left (say −). The + 1 order is more intense than − 1, + 2 more intense than − 2, and so on, each to each in the same spectrum. The difference in intensities, of + 3 and − 3 orders, for inclination marked 22′, is remarkable.

The plate was slowly turned and kept at a position corresponding to the maximum number of orders that could be obtained on the + side. The quartz plate has made an angle of 22′. It should be remarked here that the total number of diffraction spectra remains what it was for symmetrical distribution, but with this difference, that the number and the intensity distribution are not the same as before. One could very easily see visually in the above experiment that the + 1 order increases in intensity to a maximum and then falls gradually for increasing angle of the light beam to the sound wave-front. The displacement in the spectra corresponding to the maximum number of orders on the + side, was two orders; that is, the + side had increased by two, while the − side had lost two. The pattern is asymmetrical.

On still further increasing the angle to 28′, one could see that the asymmetry was maintained while progressively about the same number of orders disappeared from either side of the zero order. Even at such a large angle as 72′, the + 2 order is definitely more intense than the − 2 order and it is only at 94′ and greater angle that something like symmetry is brought about. At still greater angles, one sees only the first order spectrum getting fainter and fainter—so that finally at an inclination of 2°, even the first order has almost disappeared.

We give below the visual estimate of intensities for different orders at four inclinations only. The intensities are only relative but indicate the progressive changes accompanying the tilting of the quartz plate.

TABLE I.

Visual Estimate of Relative Intensities.

Angle of Inclination	−Order			+Order			
	5	3	1	1	3	5	7
0	1	8	20	20	8	1	0
6′	½	6	20	25	12	2	0
22′	0	3	25	30	20	6	2
28′	0	1	6	15	8	1	less than ½

An exactly similar set of changes occurred when the quartz plate was turned in the opposite direction, but now the greater number of orders was observed on the — side of the zero order, as against the + side as observed previously.

Part II. A Case of Overlapping Resonance.

While the author was experimenting, he observed a curious phenomenon. At one stage in the setting of the variable condenser, he obtained one kind of diffraction spectra, and not far from it, not more than 40° in the setting of the variable condenser, another set of spectra, with distances for the first orders in the ratio 2 : 3. At some intermediate position between the two, the two first orders were obtained simultaneously on the ground-glass plate; while turning of the condenser either way, increased the intensity of one kind or the other, depending on the direction it was turned, with consequent diminution of the other kind. This was quite unexpected, and therefore the electrical wave-length for the two resonances were determined by means of a wave-meter, to determine the exact frequency with which the quartz was oscillating.

These frequencies were again checked in the following way. Since the liquid used was benzene, we know with fair accuracy the velocity of sound in it, and from a knowledge of the angles θ_1 and θ_2 which the first order of each kind produces, it is easy to calculate the wave-length of sound in the medium and hence the frequency of oscillation of the quartz plate.

The quartz plate used was of dimensions 20 × 20 × 1 mms.

The following table gives the results obtained in the case of overlapped resonance.

TABLE II.

No.	At the point of overlapping resonance			Frequency at the resonance point	Number of the harmonic of the crystal
	Wave-length of sound in benzene in mms.	Frequency from previous column in c/s.	Frequency by wave-meter reading in c/s.	in c/s.	
1	2·000 mms.	$6{\cdot}46\times10^6$	$6{\cdot}45\times10^6$	$6{\cdot}75\times10^6$	$^5/_2\,n$
2	2·945 mms.	$9{\cdot}69\times10^6$	$9{\cdot}70\times10^6$	$9{\cdot}45\times10^6$	$^7/_2\,n$

It is evident, therefore, that the crystal is vibrating at the $\frac{5}{2}$th and $\frac{7}{2}$th harmonic of the crystal, simultaneously.

We know that in liquids the resonances are broad and the present result is a case of superposition of the base of the two resonances, occurring

near to each other. This is clear if we closely notice what happens if the condenser is turned either way. Along the reading common to both, one of the spectra should get brighter depending upon the fact how much of the curve of the other it overlaps, and then finally should reach the pure resonance of $\frac{5}{2}n$ or $\frac{7}{2}n$ where n is the fundamental of the quartz. This was realised completely in the experiment.

Fig. 3 is a photograph of the overlapped resonance, while Fig. 4 gives the true graphical representation of facts.

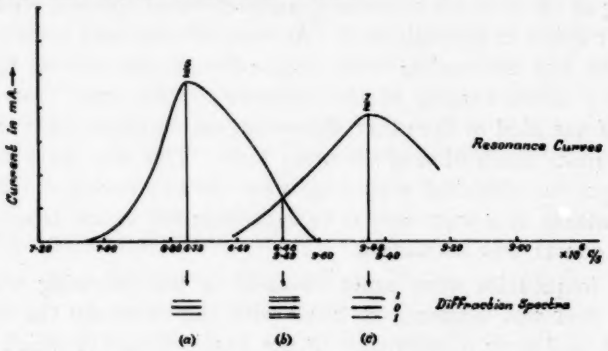

FIG. 4.

It will be worth recording here that L. Bergmann[6] observed and proved by these optical methods, the simultaneous existence of fundamentals and harmonics, and any two harmonics, and it has not been known whether such $\frac{7}{2}n$ and $\frac{5}{2}n$ are possible of excitation. It is a fact known to all in the field of radio communication that transmitters are capable, in addition to the fundamental frequency, of sending harmonics, but always with the fundamental, though feebly.

Fig. 5 reproduces the diffraction spectra due to standing waves in *p*-Xylene at 7.32×10^6 c/s. Others have reported previously, notable among them being Oyama,[7]* on the production of a large number of diffraction orders due to ultrasonic waves. The number of orders observed by the author is 16 and it will be interesting to account for such a large number and also their intensities by the Raman-Nath theory as developed in Part III. Further work is being continued in this direction.

The author thanks Professor Sir C. V. Raman for the interest he took in the work.

* Oyama's 30 orders really correspond to 15 orders; he probably means 30 lines, which will be +15 and −15 orders. Nobody seems to have obtained even as great many as 20 orders of diffraction spectra. 16 appears to be the maximum.

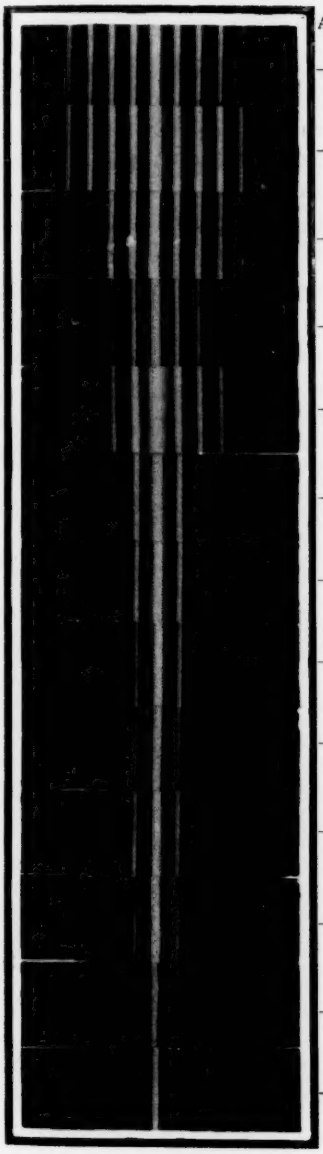

FIG. 2.

Diffraction spectra at small angles between the incident light beam and the sound wave-front.

FIG. 3.

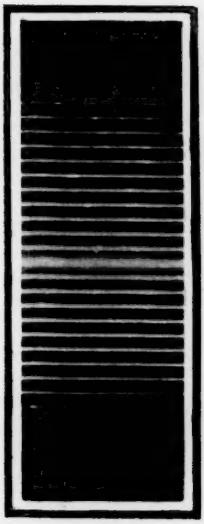

FIG. 5.

In *p*-Xylene

Summary.

A detailed relationship between the angle of inclination of the oscillating quartz, and the diffraction spectra produced by it at these angles, is given. It is explicable on the basis of the Raman-Nath theory for the diffraction of light by high-frequency sound waves. The paper includes the case of overlapped resonance, the resonances occurring at $\frac{1}{2}n$ and $\frac{1}{4}n$, independent of each other.

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NEUTRINOS AND LIGHT QUANTA.*

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1. Introduction.

Jordan who has initiated the Neutrino Theory of light has indicated that optical phenomena are really simultaneous actions of pairs of neutrinos which obey the Fermi-Dirac statistics. His investigation is of very great significance for it shows that the only primary statistics in physical phenomena is the Fermi-Dirac one with anti-symmetric wave functions. He has shown that photons which obey the Bose-Einstein statistics do not really exist at all but that they constitute only a secondary effect appearing under special circumstances; that is, the way of the interaction of the neutrinos with electric charges leads to the effect that pairs of neutrinos behave generally as photons. Recently, a report was published in these *Proceedings* by Max Born and the author on the above work of Jordan and some developments in the same subject due to Kronig. We have removed therein many of the apparent contradictions involved in their papers. The chief one of them was with regard to the spin of the neutrino. We found that there was no reason to introduce the spin of the neutrino so far as the up-to-date results of Jordan and Kronig were concerned. We had only to postulate only one kind of neutrino with positive or negative energy. That is, there was no need to distinguish between the two kinds of neutrinos for they differ in the same way as electrons and positrons in Dirac's theory of holes. The spin is a property independent of this distinction which has to be introduced separately and will be treated in this paper. The difficulties regarding the negative infinite energy were removed by introducing the idea of holes for the variables of the states as is done in Dirac's theory of holes. We also pointed out that the way of the interaction of the neutrinos with electrons could be simply formulated in the one principle that the average photon energy density of energy l is given as a Raman effect with the universal rule: Absorption of a neutrino of any (positive or negative) energy κ and the simultaneous emission of a neutrino with the energy $\kappa - l$ where $-\infty < \kappa < \infty$.

* The writing up of this paper is on similar lines as to be found in the report by Max Born and the author, *Proc. Ind. Acad. Sci.*, 1936, 3, 318. The above report is referred to in this paper as BN. References to the literature are to be found there.

It is quite definite that the idea of spin is unnecessary so far as the present Jordan-Kronig results are concerned. But the existence of the spin cannot be rejected if we examine the problem more carefully. One of the primary reasons for the existence of the spin for the neutrino is that it obeys the Fermi-Dirac statistics. Secondly, if we wish to retain the idea that the total spin is conserved in the processes of the interaction between neutrinos and electrons (or other elementary particles), we would be unable to understand the change in the spin of an electron in electron transitions influenced by the presence of the neutrinos if that change of spin does not arise from the neutrinos. In the case of electrons in atoms, we should also remember the change in the angular momentum of an atom during such processes. Born opines that a satisfying theory including the above point could only be developed by a proper treatment of the problem in three dimensions. Apart from all these reasons, there is still another vital reason to introduce the spin for the neutrino. It is that we will have to incorporate in the theory of light, the idea of polarisation and derive the Planck formula for the radiation density. The former point is as yet untouched by previous investigators while the latter point has been dealt with by Jordan but not with complete success. *Jordan's expression for the radiation density is only half of Planck's formula for Jordan's photons have no polarisation properties.* In the following paper these difficulties have been removed by a proper treatment of the spin of the neutrino.

It is the purpose of this paper to introduce the spin of the neutrino and to show that we get two different photon operators for photons with the same energy and thus obtain the Planck formula for the density of radiation.

2. Neutrino Operators and their Jordan-Wigner Representations.

Two infinite sets of non-commuting variables $a_{\kappa,i}$, $\gamma_{\kappa,i}$ are chosen as the operators describing the neutrinos, where κ takes all the positive half integral numbers $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$ and i takes the only two values R and I, which characterise the two spin states. We introduce operators with negative indices defined as follows:—

$$(1)\quad a_{-\kappa,i} = \gamma_{\kappa,i}^{\dagger}\,; \quad \gamma_{-\kappa,i} = a_{\kappa,i}^{\dagger} \qquad \kappa > 0.$$

The above operators obey the following commutation rules.

$$(2)\quad \begin{aligned} &a_{\kappa,i}\, a_{\mu,j} + a_{\mu,j}\, a_{\kappa,i} = 0 \\ &\gamma_{\kappa,i}\, \gamma_{\mu,j} + \gamma_{\mu,j}\, \gamma_{\kappa,i} = 0 \\ &\gamma_{\kappa,i}\, a_{\mu,j} + a_{\mu,j}\, \gamma_{\kappa,i} = \delta_{\mu,-\kappa}\, \delta_{i,j}. \end{aligned}$$

The operators describing the number of neutrinos and anti-neutrinos of energy κ, $(\kappa > o)$ are defined by the following operators.

$$(3)\quad \begin{aligned} &N_{\kappa,i}^{(+)} = a_{\kappa,i}^{\dagger}\, a_{\kappa,i} = 1 - a_{\kappa,i}\, a_{\kappa,i}^{\dagger} \\ &N_{\kappa,i}^{(-)} = \gamma_{\kappa,i}^{\dagger}\, \gamma_{\kappa,i} = 1 - \gamma_{\kappa,i}\, \gamma_{\kappa,i}^{\dagger} \end{aligned}$$

As in BN, we can write down the Jordan-Wigner representation of the neutrino operators by the following scheme.

(4)
$\kappa > 0$

	$\frac{1}{2}, R$;	$\frac{1}{2}, L$;	$-\frac{1}{2}, R$;	$-\frac{1}{2}, L$;	---- ;	κ, R ;	κ, L ;	$-\kappa, R$;	$-\kappa, L$;	----
$a_{\kappa,R} = \gamma_{-\kappa,R}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$a_{\kappa,L} = \gamma_{-\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$a_{-\kappa,R} = \gamma_{\kappa,R}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$a_{-\kappa,L} = \gamma_{\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$\gamma_{\kappa,R} = a_{-\kappa,R}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$\gamma_{\kappa,L} = a_{-\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$\gamma_{-\kappa,R} = a_{\kappa,R}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$
$\gamma_{-\kappa,L} = a_{\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	s	$\times$	s	$\times$	----	$\times$

	κ, R ;	κ, L ;	$-\kappa, R$;	$-\kappa, L$;	----
$a_{\kappa,R} = \gamma_{-\kappa,R}^{\dagger}$	a	$\times$	1	$\times$	----
$a_{\kappa,L} = \gamma_{-\kappa,L}^{\dagger}$	s	$\times$	1	$\times$	----
$a_{-\kappa,R} = \gamma_{\kappa,R}^{\dagger}$	s	$\times$	$a^{\dagger}$	$\times$	----
$a_{-\kappa,L} = \gamma_{\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	----
$\gamma_{\kappa,R} = a_{-\kappa,R}^{\dagger}$	s	$\times$	a	$\times$	----
$\gamma_{\kappa,L} = a_{-\kappa,L}^{\dagger}$	s	$\times$	s	$\times$	a ----
$\gamma_{-\kappa,R} = a_{\kappa,R}^{\dagger}$	$a^{\dagger}$	$\times$	1	$\times$	----
$\gamma_{-\kappa,L} = a_{\kappa,L}^{\dagger}$	s	$\times$	1	$\times$	----

where

$$(5) \qquad a = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}; \; s = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

and the sign of multiplication refers to the symbol of direct product of matrices defined in BN.

Each matrix has only one non-vanishing element given by the following scheme in which $t_{\kappa,i}$ is zero or unity.

(6)

$$a_{\kappa,\mathrm{R}}\ (---,\ 0,\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ ---\ ;\ ---,\ 1,\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{-(\kappa-1),\mathrm{L}}}$$

$$a_{\kappa,\mathrm{L}}\ (---,\ t_{\kappa,\mathrm{R}},\ 0,\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ ---\ ;\ ---,\ t_{\kappa,\mathrm{R}},\ 1,\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{\kappa,\mathrm{R}}}$$

$$a_{-\kappa,\mathrm{R}}\ (---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ 1,\ t_{-\kappa,\mathrm{L}},\ ---\ ;\ ---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ 0,\ t_{-\kappa,\mathrm{L}},\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{\kappa,\mathrm{L}}}$$

$$a_{-\kappa,\mathrm{L}}\ (---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ 1,\ ---\ ;\ ---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ 0,\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{-\kappa,\mathrm{R}}}$$

$$\gamma_{\kappa,\mathrm{R}}\ (---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ 0,\ t_{-\kappa,\mathrm{L}},\ ---\ ;\ ---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ 1,\ t_{-\kappa,\mathrm{L}},\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{\kappa,\mathrm{L}}}$$

$$\gamma_{\kappa,\mathrm{L}}\ (---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ 0,\ ---\ ;\ ---,\ t_{\kappa,\mathrm{R}},\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ 1,\ ---)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{-\kappa,\mathrm{R}}}$$

$$\gamma_{-\kappa,\mathrm{R}}\ (---,\ 1,\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ --\ ;\ ---,\ 0,\ t_{\kappa,\mathrm{L}},\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ --)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{-(\kappa-1),\mathrm{L}}}$$

$$\gamma_{-\kappa,\mathrm{L}}\ (---,\ t_{\kappa,\mathrm{R}},\ 1,\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ --\ ;\ --,\ t_{\kappa,\mathrm{R}},\ 0,\ t_{-\kappa,\mathrm{R}},\ t_{-\kappa,\mathrm{L}},\ --)$$
$$= (-)^{t_{\frac{1}{2},\mathrm{R}}+--+t_{\kappa,\mathrm{R}}}$$

3. *A New System of Operators.*

As in BN, we introduce operators $a_{\kappa,i}$ and $c_{\kappa,i}$ defined by

(7)*
$$a_{\kappa,i} = \frac{a_{\kappa,i}+\gamma_{\kappa,i}}{\sqrt{2}}\ ;$$
$$c_{\kappa,i} = \frac{a_{\kappa,i}-\gamma_{\kappa,i}}{i\sqrt{2}}.$$

We can express $a_{\kappa,i}$ and $\gamma_{\kappa,i}$ as functions of $a_{\kappa,i}$ and $c_{\kappa,i}$ as

(8)
$$a_{\kappa,i} = \frac{a_{\kappa,i}+i\,c_{\kappa,i}}{\sqrt{2}}\ ;$$
$$\gamma_{\kappa,i} = \frac{a_{\kappa,i}-i\,c_{\kappa,i}}{\sqrt{2}}.$$

It can be easily found from (7) and (1) that

(9) $\quad a_{-\kappa,i} = a_{\kappa,i}{}^{\dagger}\ ; \qquad c_{-\kappa,i} = c_{\kappa,i}{}^{\dagger}.$

---

*No confusion should be made in i which characterises the spin states occurring in the suffixes and which denotes $\sqrt{-1}$ otherwise.

Also, a's and c's can be seen to obey the following commutation rules with the help of (2) and (8).

$$(10)\quad \begin{aligned} a_{\kappa,i}\, a_{\mu,j} + a_{\mu,j}\, a_{\kappa,i} &= \delta_{\mu,-\kappa}\, \delta_{i,j} \\ c_{\kappa,i}\, c_{\mu,j} + c_{\mu,j}\, c_{\kappa,i} &= \delta_{\mu,-\kappa}\, \delta_{i,j} \\ a_{\kappa,i}\, c_{\mu,j} + c_{\mu,j}\, a_{\kappa,i} &= 0 \end{aligned}$$

for $\kappa,\mu = \pm \tfrac{1}{2}, \pm \tfrac{3}{2}, \ldots$ and $i, j = \mathrm{R}, \mathrm{L}$.

We define the operators $\mathrm{L}_{\kappa,i}$ and $\mathrm{N}_{\kappa,i}$ to be given by

$$(11)\quad \mathrm{L}_{\kappa,i} = a_{\kappa,i}^{\dagger}\, a_{\kappa,i}\,; \quad \mathrm{N}_{\kappa,i} = c_{\kappa,i}^{\dagger}\, c_{\kappa,i}.$$

It will be quite easy to see that

$$(12)\quad \begin{aligned} \mathrm{L}_{\kappa,i} + \mathrm{N}_{\kappa,i} &= \mathrm{N}_{\kappa,i}^{(+)} + \mathrm{N}_{\kappa,i}^{(-)}, \\ \mathrm{L}_{\kappa,i} - \mathrm{N}_{\kappa,i} &= a_{\kappa,i}^{\dagger}\, \gamma_{\kappa,i} + \gamma_{\kappa,i}^{\dagger}\, a_{\kappa,i}. \end{aligned}$$

Under the same considerations as in BN, we can show that

$$(13)\quad \Sigma\, \mathrm{L}_{\kappa,i} \quad \text{and} \quad \Sigma\, \mathrm{N}_{\kappa,i}$$

are convergent.

4. *The Operators describing the Photon States.*

For each energy state k we introduce two operators defined by

$$(14a)\quad \boxed{b_{k,\rho} = \frac{i}{\sqrt{\,|\,2k\,|\,}} \sum_{\kappa=-\infty}^{\infty} \sum_{i} a_{\kappa,i}\, c_{k-\kappa,i}}$$

and

$$(14b)\quad \boxed{b_{k,\lambda} = \frac{i}{\sqrt{\,|\,2k\,|\,}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j}{}' a_{\kappa,i}\, c_{k-\kappa,j}}$$

for $k = \pm 1, \pm 2, \pm 3, \ldots$, where the dash over the (i, j) summation sign indicates that $i \neq j$.

It may be easily found that

$$(15)\quad b_{k,\iota}^{\dagger} = b_{-k,\iota} \quad \text{where } \iota = \rho, \lambda.$$

We can find expressions for these new operators in terms of a's and γ's. They are

$$(16)\quad \boxed{\begin{aligned} b_{k,\rho} &= \frac{-1}{\sqrt{\,|\,2k\,|\,}} \sum_{\kappa=-\infty}^{\infty} \sum_{i} a_{\kappa,i}\, \gamma_{k-\kappa,i} \\ b_{k,\lambda} &= \frac{-1}{\sqrt{|2k|}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j}{}' a_{\kappa,i}\, \gamma_{k-\kappa,j} \end{aligned}}$$

We also introduce two operators B_ρ and B_λ defined by

$$
\begin{aligned}
B_\rho &= \frac{i}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_i a_{\kappa,i}\, c_{-\kappa,i} = \frac{1}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_i (a_{\kappa,i}^\dagger\, a_{\kappa,i} - \gamma_{\kappa,i}^\dagger \gamma_{\kappa,i}) \\
B_\lambda &= \frac{i}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j}{}' a_{\kappa,i}\, c_{-\kappa,j} = \frac{1}{\sqrt{2}} \sum_{\kappa=-\infty}^{\infty} \sum_{i,j}{}' (a_{\kappa,i}^\dagger\, a_{\kappa,j} - \gamma_{\kappa,i}^\dagger \gamma_{\kappa,j})
\end{aligned} \tag{17}
$$

We will now examine the commutability of these operators defined by (14) and (10).*

$$
\begin{aligned}
(a)\quad [b_{r,\rho},\, b_{s,\rho}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_{u,v} (a_{m,u}\, c_{s-m,u}\, a_{l,v}\, c_{r-l,v} \\
&\qquad - a_{l,v}\, c_{r-l,v}\, a_{m,u}\, c_{s-m,u}) \\
&= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_u (a_{l,u}\, a_{-l+r+s,u} - c_{l+s,u}\, c_{r-l,u}) \\
&= 0 \text{ if } r+s \neq 0, \\
&= 1 \text{ if } r+s = 0, \quad r > 0. \\
(b)\quad [b_{r,\lambda},\, b_{s,\lambda}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_{u,v}{}' \sum_{i,j}{}' (a_{m,u}\, c_{s-m,v}\, a_{l,i}\, c_{r-l,j} \\
&\qquad - a_{l,i}\, c_{r-l,j}\, a_{m,u}\, c_{s-m,v}) \\
&= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_i (a_{l,i}\, a_{-l+r+s,i} - c_{s+l,i}\, c_{r-l,i}) \\
&= 0 \text{ if } r+s \neq 0, \\
&= 1 \text{ if } r+s = 0, \quad r > 0. \\
(c)\quad [b_{r,\rho},\, b_{s,\lambda}] &= \frac{1}{2\sqrt{|rs|}} \sum_{l,m} \sum_i \sum_{u,v}{}' (a_{m,u}\, c_{s-m,v}\, a_{l,i}\, c_{r-l,i} \\
&\qquad - a_{l,i}\, c_{r-l,i}\, a_{m,u}\, c_{s-m,v}) \\
&= \frac{1}{2\sqrt{|rs|}} \sum_l \sum_{i,j}{}' (a_{l,i}\, a_{-l+r+s,j} - c_{s+l,i}\, c_{r-l,j}) \\
&= 0 \\
(d)\quad [B_\lambda,\, b_{r,\lambda}] &= \frac{1}{2\sqrt{|r|}} \sum_{l,m} \sum_{i,j}{}' \sum_{u,v}{}' (a_{m,u}\, c_{r-m,v}\, a_{l,i}\, c_{-l,j} \\
&\qquad - a_{l,i}\, c_{-l,j}\, a_{m,u}\, c_{r-m,v}) \\
&= \frac{1}{2\sqrt{|r|}} \sum_l \sum_{i,j}{}' (a_{l,i}\, a_{r-l,j} - c_{r+l,i}\, c_{-l,j}) \\
&= 0 \\
(e)\quad [B_\rho,\, b_{r,\lambda}] &= \frac{1}{2\sqrt{|r|}} \sum_{l,m} \sum_i \sum_{u,v}{}' (a_{m,u}\, c_{r-m,v}\, a_{l,i}\, c_{-l,i} \\
&\qquad - a_{l,i}\, c_{-l,i}\, a_{m,u}\, c_{r-m,v}) \\
&= 0
\end{aligned}
$$

---

* As in BN, we assume that the series

$$\Sigma a_{-\kappa+r,i}\, a_{\kappa,i} \text{ and } \Sigma c_{-\kappa+r,i}\, c_{\kappa,i}$$

are convergent for any finite r. Refer BN for further details.

$$(f)\quad [B_\lambda, b_{r,\rho}] = 0$$
$$(g)\quad [B_\rho, b_{r,\rho}] = 0$$
$$(h)\quad [B_\rho, B_\lambda] = 0$$

Thus

$$(18)\qquad \boxed{\begin{aligned} &b_{r,\iota}\, b_{s,\sigma} - b_{s,\sigma}\, b_{r,\iota} = \delta_{r,-s}\, \delta_{\iota,\sigma} \\ &B_\iota\, b_{r,\sigma} - b_{r,\sigma} B_\iota = 0 \\ &B_\rho\, B_\lambda - B_\lambda\, B_\rho = 0 \end{aligned}}$$

for $\iota, \sigma = \rho, \lambda$ and $r > 0$.

5. *Photons and Statistical Equilibrium.*

The photons in a hohlraum can be represented by a set of variables $b_{k,\iota}$ which satisfy the commutation rules (18). For a state with given number of neutrinos $N^{(+)}$ and $N^{(-)}$ the operators representing the number of photons in the k *th* energy state with the indices ρ, λ are

$$(19)\quad P_{k,\rho} = b_{k,\rho}^{\dagger}\, b_{k,\rho}\,; \quad P_{k,\lambda} = b_{k,\lambda}^{\dagger}\, b_{k,\lambda}.$$

The average value of the number of photons with energy k is

$$(20)\quad \bar{P}_k = \bar{P}_{k,\rho} + \bar{P}_{k,\lambda} = \sum_{t_{\frac{1}{2},R}', t_{\frac{1}{2},L}', t_{-\frac{1}{2},R}', t_{-\frac{1}{2},L}'} \left\{ \begin{matrix} |\, b_{k,\rho}\,(t_{\frac{1}{2},R}', \text{---}; t_{\frac{1}{2},R}, \text{---})\,|^2 \\ +\,|\, b_{k,\lambda}\,(t_{\frac{1}{2}R}', \text{---}; t_{\frac{1}{2},R}, \text{---})\,|^2 \end{matrix} \right\}$$

Just as in BN, we can show that

$$(21)\quad \begin{aligned} \bar{P}_k = {} & \frac{1}{2k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} \sum_i N_{\kappa,i}^{(+)}\, N_{k-\kappa,i}^{(-)} + \frac{1}{2k} \sum_{\frac{1}{2}}^{\infty} \sum_i \{N_{k+\kappa,i}^{(+)}\,(1 - N_{\kappa,i}^{(+)}) \\ & + N_{k+\kappa,i}^{(-)}\,(1 - N_{\kappa,i}^{(-)})\} \\ & + \frac{1}{2k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} \sum_{i,j}' N_{\kappa,i}^{(+)}\, N_{k-\kappa,j}^{(-)} + \frac{1}{2k} \sum_{\frac{1}{2}}^{\infty} \sum_{i,j}' \{N_{k+\kappa,i}^{(+)}\,(1 - N_{\kappa,j}^{(+)}) \\ & N_{k+\kappa,i}^{(-)}\,(1 - N_{\kappa,j}^{(-)})\} \end{aligned}$$

We will now assume that the average number of neutrinos of energy κ in the R state is equal to the average number of neutrinos of energy κ in the L state. Thus

$$(22)\quad \begin{aligned} &N_{\kappa,R}^{(+)} = N_{\kappa,L}^{(+)} = N_\kappa^{(+)}\,; \\ &N_{\kappa,R}^{(-)} = N_{\kappa,L}^{(-)} = N_\kappa^{(-)}, \end{aligned}$$

so that

$$(23)\quad \bar{P}_k = \frac{2}{k} \sum_{\frac{1}{2}}^{k-\frac{1}{2}} N_\kappa^{(+)}\, N_{k-\kappa}^{(-)} + \frac{2}{k} \sum_{\frac{1}{2}}^{\infty} \{N_{k+\kappa}^{(+)}\,(1 - N_\kappa^{(+)}) + N_{k+\kappa}^{(-)}\,(1 - N_\kappa^{(-)})\}.$$

We can show that

$$(24)\quad N_l^{(+)} = \frac{ay}{1+ay} \text{ and } N_l^{(-)} = \frac{y/a}{1+y/a}$$

where $y = e^{-\beta l}$ and $\beta = h\nu_1 / kT$.

Following the same procedure as in BN, we find

$$(25)\quad \overline{P(\nu)} = \frac{2}{e^{h\nu/kT} - 1}.$$

If we assume that the density of radiation with frequency lying between ν and $\nu + d\nu$ is

$$(26)\quad \frac{4\pi\nu^2 d\nu}{c^3} h\nu \, (\bar{P}_{r,\rho} + \bar{P}_{r,\lambda}), \quad r\nu_1 = \nu$$

we get the density of radiation to be*

$$(27)\quad \frac{4\pi\nu^2 d\nu}{c^3} h\nu \, \overline{P(\nu)} = \frac{8\pi\nu^2 d\nu}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

which is the Planck formula for the radiation density.

6. Jordan's Derivation of the Formula for the Radiation Density.

According to Jordan

$$\overline{P(\nu)} = \frac{1}{e^{h\nu/kT} - 1}.$$

The number of radiation oscillators per unit volume is

$$\frac{4\pi\nu^2 d\nu}{c^3}$$

as the photons defined by Jordan have no polarisation properties. Therefore, Jordan has effectively got only half of Planck's formula. Even if we restrict our considerations to one dimensional hohlraum this difficulty does not disappear.

7. Relation between the Energy of Neutrinos and Photons.

The energy of photons (in units of $h\nu_1$, ν_1 being the fundamental frequency of the hohlraum) is given by

$$(28)\quad \begin{aligned} W &= W_\rho + W_\lambda \\ &= \sum_k k \, (P_{k,\rho} + P_{k,\lambda}) \end{aligned}$$

---

* In three dimensions, we assume that (25) is the same for all the states with frequency ν.

The energy of neutrinos in the same units is given by

$$(29)\quad \begin{aligned} E &= E_R + E_L \\ &= \sum_k \sum_i k\,(L_{k,i} + N_{k,i}), \quad i = R,L. \end{aligned}$$

$$W_\rho = -\tfrac{1}{2} \sum_{\substack{l,m \\ -\infty}}^{\infty} \sum_{i,u} \sum_{k\,1}^{\infty} a_{l,i}\, c_{-k-l,i}\, a_{m,u}\, c_{k-m,u}$$

$$(30)\quad = \tfrac{1}{2} \sum_{\substack{l,m \\ -\infty}}^{\infty}{}'' \sum_{k\,1}^{\infty} \sum_{i,j}'' a_{l,i}\, a_{m,j}\, c_{-k-l,i}\, c_{k-m,j} + \tfrac{1}{2} \sum_{l\,-\infty}^{\infty} \sum_i \sum_{k\,1}^{\infty} a_{l,i}\, a_{-l,i}\, c_{-k-l,i}\, c_{k+l,i}$$

where the double dashes over the (l, m) and (i, j) summations indicate that $l \neq -m$ and $i \neq j$ simultaneously. Changing in the first summation k to $-k$, l to m, m to l, i to j, j to i and using the commutation rules (10), we get

$$(31)\quad W_\rho = \tfrac{1}{2} \sum_{\substack{l,m \\ -\infty}}^{\infty}{}'' \sum_{k\,-1}^{\infty} \sum_{i,j}'' a_{l,i}\, a_{m,j}\, c_{-k-l,i}\, c_{k-m,j} + \tfrac{1}{2} \sum_{l\,-\infty}^{\infty} \sum_{k\,1}^{\infty} \sum_i a_{l,i}\, a_{-l,i}\, c_{-k-l,i}\, c_{k+l,i}$$

But

$$(32)\quad B_\rho^2 = \tfrac{1}{2} \sum_{\substack{l,m \\ -\infty}}^{\infty}{}'' \sum_{i,j}'' a_{l,i}\, a_{m,j}\, c_{-l,i}\, c_{-m,j} + \tfrac{1}{2} \sum_{l\,-\infty}^{\infty} \sum_i a_{l,i}\, a_{-l,i}\, c_{-l,i}\, c_{l,i}$$

Adding (30), (31) and (32), we get

$$(33)\quad \begin{aligned} 2W_\rho + B_\rho^2 = \tfrac{1}{2} &\sum_{\substack{l,m \\ -\infty}}^{\infty}{}'' \sum_{k\,-\infty}^{\infty} \sum_{i,j}'' a_{l,i}\, a_{m,j}\, c_{-k-l,i}\, c_{k-m,j} \\ &+ \sum_{l\,-\infty}^{\infty} \sum_i \sum_{k\,1}^{\infty} a_{l,i}\, a_{-l,i}\, c_{-k-l,i}\, c_{k+l,i} + \tfrac{1}{2} \sum_l \sum_i a_{l,i}\, a_{-l,i}\, c_{-l,i}\, c_{l,i} \end{aligned}$$

Similarly

$$(34)\quad \begin{aligned} 2W_\lambda + B_\lambda^2 = \tfrac{1}{2} &\sum_{\substack{l,m \\ -\infty}}^{\infty}{}'' \sum_{k\,-\infty}^{\infty} \sum_{i,j}'' \sum_{u,v}^{*} a_{l,i}\, a_{m,j}\, c_{-k-l,u}\, c_{k-m,v} \\ &+ \sum_{l\,-\infty}^{\infty} \sum_{ij}' \sum_{k\,1}^{\infty} a_{l,i}\, a_{-l,i}\, c_{-k-l,j}\, c_{k+l,j} \\ &+ \tfrac{1}{2} \sum_l \sum_{i,j}' a_{l,i}\, a_{-l,i}\, c_{-l,j}\, c_{l,j} \end{aligned}$$

where the star over the (u, v) summation indicates that $i \neq u$ and $j \neq v$. Thus, adding (33) and (34), we get

$$2\,(W_\rho + W_\lambda) + (B_\rho^2 + B_\lambda^2)$$

$$= \tfrac{1}{2} \sum_{\substack{l,m \\ -\infty\,-\infty}}^{\infty}{}'' \sum_{k}^{\infty} \sum_{i,j}'' \sum_{u,v}^{*} a_{l,i}\, a_{m,j}\, (c_{-k-l,i}\, c_{k-m,j} + c_{-k-l,u}\, c_{k-m,v})$$

$$(35)\qquad + \sum_{-\infty}^{l} \sum_{1}^{\infty} \sum_{i,j}' a_{l,i}\, a_{-l,i}\, (c_{-k-l,i}\, c_{k+l,i} + c_{-k-l,j}\, e_{k+l,j})$$

$$+ \sum_{-\infty}^{l} \sum_{i,j}' a_{l,i}\, a_{-l,i}\, (c_{-l,i}\, c_{l,i} + c_{-l,j}\, c_{l,j}).$$

In the first summation, if we add the kth term to $(-k-l+m)$th term we get zero. Therefore, the whole sum is zero.

$$\therefore\ 2(W_\rho + W_\lambda) + B_\rho^2 + B_\lambda^2$$

$$= \sum_{-\infty}^{l} \sum_{1}^{\infty} \sum_{i,j} a_{l,i}\, a_{-l,i}\, c_{-k-l,j}\, c_{k+l,j}$$

$$+ \tfrac{1}{2} \sum_{-\infty}^{l} \sum_{i,j} a_{l,i}\, a_{-l,i}\, c_{-l,j}\, c_{l,j}$$

$$= \sum_{\frac{1}{2}}^{\infty} \sum_{i} (1 - L_{l,i}) \sum_{1}^{\infty} \sum_{j} N_{k+l,j} + \sum_{3/2}^{\infty} \sum_{i} L_{l,i} \sum_{1}^{l-\frac{1}{2}} \sum_{j} (1 - N_{-k+l,j})$$

$$+ \sum_{3/2}^{\infty} \sum_{i} L_{l,i} \sum_{l+\frac{1}{2}}^{\infty} \sum_{j} N_{k-l,j} + \sum_{i} L_{\frac{1}{2},i} \sum_{1}^{\infty} \sum_{j} N_{k-\frac{1}{2},j}$$

$$+ \tfrac{1}{2} \sum_{\frac{1}{2}}^{\infty} \sum_{i} (1 - L_{l,i}) \sum_{j} N_{l,j} + \tfrac{1}{2} \sum_{\frac{1}{2}}^{\infty} \sum_{i} L_{l,i} \sum_{j} (1 - N_{l,j})$$

$$(36)\qquad = 2 \sum_{\frac{1}{2}}^{\infty} \sum_{i} l\, (L_{l,i} + N_{l,i}) = 2\,(E_R + E_L)$$

Thust

$$(37a)\qquad \boxed{2\,(W_\rho + W_\lambda) + (B_\rho^2 + B_\lambda^2) = 2\,(E_R + E_L)}$$

$$(37b)\qquad \therefore \qquad \boxed{E - W = \frac{B_\rho^2 + B_\lambda^2}{2}}$$

A pure photon state would correspond to

$$B_\rho = 0; \qquad B_\lambda = 0.$$

A pure neutrino state would correspond to

$$W = 0.$$

---

† It should be remembered that the energy is expressed in units of $h\nu_1$.

7. *Conclusion.*

It is found necessary in this paper to introduce the spin of the neutrino in the neutrino theory of light in order to obtain two photon operators for each energy state of photons and derive the Planck formula. The derivation by Jordan without the idea of spin for the neutrino is not free from objection for he obtains half the Planck formula for the radiation density for his photons have no polarisation states. This difficulty disappears in our derivation of the Planck formula for we obtain two photon operators for each energy state of photons. These two operators are connected with the polarisation states of light.

The author is highly grateful to Prof. Dr. Max Born for the very valuable discussions during his stay here and for his very kind correspondence. He is also grateful to Professor C. V. Raman for his interest in this work.

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES : PART V.

General Considerations—Oblique Incidence and Amplitude Changes.

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1. Introduction.

The essential idea that the phenomenon of the diffraction of light by high frequency sound waves depends on the corrugated form of the wave-front of the transmitted light has been pointed out by us in Part I of this series of papers.[1] Therein, we considered that the corrugated wave-front of light could be simply obtained by considering the phase changes accompanying the traversing beam which was assumed to undergo no amplitude changes at its various points. This course was adopted by us to bring out the essential features of the theory without unnecessary complications. By a close study of the problem, one can however easily see that the consideration of the phase changes is far more important than the amplitude changes if we desire to understand the essential features of the phenomenon. Indeed, this fact holds if we consider the case when the sound wave field is small and the wave-length of sound is large. This has been experimentally confirmed quite recently by Bär.[2]

In Part IV of this series of papers, we proposed the method of obtaining the wave function of light by considering the partial differential equation governing the propagation of light in a medium filled with sound waves. *Such a procedure would naturally take account of both the amplitude changes and the phase changes accompanying the beam.* These changes should be however periodic in character. On these considerations we found that, in the case of a progressive sound wave, the nth order diffraction component will be inclined at an angle $\sin^{-1}(-n\lambda/\lambda^*)$ to the direction of propagation of the incident light and will have the frequency $\nu - n\nu^*$ where ν and λ denote the frequency and the wave-length of the incident light while ν^* and λ^* correspond to those of the sound wave. We also showed that when the disturbance in the medium is simple harmonic, the relative intensity of the

nth order is given by $|\phi_n|^2$ where ϕ_n is the solution of the equation

$$(1)\quad \mu^2 \frac{d^2\phi_n}{d\xi^2} - 2i\mu_0\mu \frac{d\phi_n}{d\xi} - \frac{n^2\lambda^2}{\lambda^{*2}}\phi_n = -\mu_0\mu i\,(\phi_{n-1} - \phi_{n+1})$$

where $\xi = 2\pi\mu z/\lambda$, μ_0 is the refractive index of the undisturbed medium, μ is the amplitude of the variation of the refractive index and the z-axis is along the direction of propagation of the incident light. As μ is of the order 10^{-5} and μ is of the order of unity, we could consider the equation for ϕ_n as given by

$$(2)\quad \boxed{2\frac{d\phi_n}{d\xi} - (\phi_{n-1} - \phi_{n+1}) = \frac{in^2\lambda^2}{\mu_0\mu\lambda^{*2}}\phi_n}$$

In the case of a stationary sound wave, we obtained the result that, in any even order, radiations with frequencies $\nu \pm 2r\nu^*$ would be present, while in any odd order, radiations with frequencies $\nu \pm \overline{2r+1}\,\nu^*$ would be present. These results interpret the experimental results of Bär[2] regarding the coherence phenomena among the diffracted orders. If the disturbance in the medium is simple harmonic, we obtained the result that the amplitudes of the various components of the nth order are given by the Fourier analysis of $g_n(\xi, t)$ which satisfies the equation

$$(3)\quad \boxed{2\frac{\partial g_n}{\partial \xi} - \sin\epsilon\,(g_{n-1} - g_{n+1}) = \frac{in^2\lambda^2}{\mu_0\mu\lambda^{*2}}g_n}$$

where $\epsilon = 2\pi\nu^* t$ and the term containing the second derivative of g_n is omitted as its coefficient is very small. *If one however ignores the spectral character of each order*, then the relative intensity of the nth order is given by

$$(4)\quad \int_0^{2\pi} |g_n(\xi, \epsilon)|^2\, d\epsilon.$$

These results pertain to the case of the incident light falling normally on the sound waves. One of the purposes of this paper is to extend the above considerations to the case of the oblique incidence of light to the sound waves. We have found that, in the case of oblique incidence, the intensity of the nth order need not be equal to that of the $-n$th order, thus explaining the results of Debye and Sears,[3] Lucas and Biqard,[4] Bär and Parthasarathy.[5] We have also investigated the amplitude changes accompanying the traversing wave-front explaining the results of Hiedemann,[7] Bär[2] and Lucas.[6]

2. *The Diffraction of Light when it is Incident Obliquely to the Sound Waves.*

We choose the axes of reference such that the x-axis points to the direction of propagation of the sound waves and the z-axis lies in the plane contained by the directions of propagation of the sound and the incident light waves. With the same considerations as in Part IV, the wave function of the light traversing the medium is given by

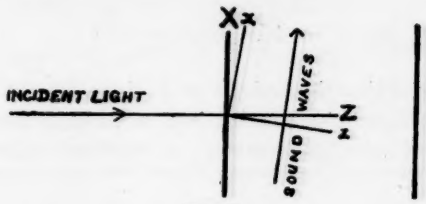

FIG. 1.

$$(5)\quad \psi = \exp(2\pi i \nu t)\,\Phi(x, z, t),$$

where Φ satisfies the equation

$$(6)\quad \frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\{\mu(x, t)\}^2\Phi.$$

Let cos ϕ and sin ϕ be the z- and x-direction cosines of the direction of propagation of the incident light. The transmitted wave travelling in the medium will suffer periodic fluctuations in its phase and amplitude with the period λ^* sec ϕ along the line in the incident plane of light and the xz plane. Thus,

$$(7)\quad \Phi(x, z, t) = \Phi(x + p\lambda^*, z - p\lambda^* \tan\phi, t).$$

So, the wave travelling in the medium is given by

$$(8)\quad e^{2\pi i\nu t} \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(x\sin\phi + z\cos\phi)\, e^{2\pi i r(x\cos\phi - z\sin\phi)/\lambda^* \sec\phi}\, e^{2\pi i s\nu^* t}$$

We choose a new axis of reference defined by

$$(9)\quad \begin{aligned} X &= x\cos\phi - z\sin\phi \\ Z &= x\sin\phi + z\cos\phi \end{aligned}$$

The new Z-axis is along the direction of propagation of the incident light. In the new system of reference, the wave function has to be written as

$$(10)\quad e^{2\pi i\nu t} \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(Z)\, e^{2\pi i r X\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}$$

Then

$$(11)\quad \Phi = \sum_{-\infty}^{\infty}\sum_{-\infty}^{\infty} f_{rs}(Z)\, e^{2\pi i r X\cos\phi/\lambda^*}\, e^{2\pi i s\nu^* t}$$

In the case of a progressive sound wave

(12) $\Phi\,(\mathrm{X} + \rho\lambda^* \sec\phi,\ \mathrm{Z},\ t) = \Phi\,(\mathrm{X},\ \mathrm{Z},\ t - \rho/\nu^*)$

This condition restricts the number of terms in the above expansion (11) so that

(13) $$\Phi = \sum_{-\infty}^{\infty} f_r\,(\mathrm{Z})\ e^{2\pi i r\,\mathrm{X}\cos\phi/\lambda^*}\ e^{-2\pi i r\nu^* t}$$

Thus

(14) $$\psi = \sum_{-\infty}^{\infty} f_r(\mathrm{Z})\ e^{2\pi i r\,\mathrm{X}\,\cos\phi/\lambda^*}\ e^{2\pi i\,(\nu - r\nu^*)\,t}$$

If one considers the diffraction effects of ψ given by (14), it will be fairly obvious that the nth order will be inclined at an angle $\sin^{-1}(-n\lambda\cos\phi/\lambda^*)$ to the Z-axis and will have the frequency $\nu - n\nu^*$ with the relative intensity expression $|\,f_n\,(\mathrm{Z})\,|^2$.

3. *The Case when the Disturbance in the Medium is Simple Harmonic.*

If we suppose that the variation in the refractive index of the medium is simple harmonic along the x-axis, it can be represented as

$$\mu\,(x,\ t) - \mu_0 = \mu\sin 2\pi\,(\nu^* t - x/\lambda^*)$$

(15) $$= -\frac{\mu}{2i}\{e^{i(bx - \epsilon)} - e^{-i(bx - \epsilon)}\}$$

$$= -\frac{\mu}{2i}\{e^{i(b\,\mathrm{X}\cos\phi + \mathrm{Z}\sin\phi - \epsilon)} - e^{-i\,(b\,\mathrm{X}\cos\phi + \mathrm{Z}\sin\phi - \epsilon}\}$$

where $\epsilon = 2\pi\nu^* t$ and $b = 2\pi/\lambda^*$.

We know from (6) that Φ satisfies the equation

$$\frac{\partial^2\Phi}{\partial x^2} + \frac{\partial^2\Phi}{\partial z^2} = -\frac{4\pi^2}{\lambda^2}\{\mu\,(x,\ t)\}^2\,\Phi$$

(16) or

$$\frac{\partial^2\Phi}{\partial \mathrm{X}^2} + \frac{\partial^2\Phi}{\partial \mathrm{Z}^2} = -\frac{4\pi^2}{\lambda^2}\{\mu\,(\mathrm{X},\ \mathrm{Z},\ t)\}^2\,\Phi$$

Substituting the Fourier series (13) and the expression (15) for $\mu\,(\mathrm{X},\ \mathrm{Z},\ t)$ in the equation (16) and neglecting the second order term with the coefficient μ^2, we get by comparing the coefficients

(17) $$\frac{d^2 f_r}{d\mathrm{Z}^2} - \frac{4\pi^2 r^2\cos^2\phi}{\lambda^{*2}}\,f_r - \mathrm{A}\,f_r =$$

$$\frac{\mathrm{B}}{2i}\{f_{r-1}\,e^{ib\mathrm{Z}\sin\phi} - f_{r+1}\,e^{-ib\mathrm{Z}\sin\phi}\}$$

where $\mathrm{A} = -4\pi^2\mu_0^2/\lambda^2$ and $\mathrm{B} = 8\pi^2\mu_0\mu/\lambda^2$.

Putting $f_r(Z) = \exp(-iu\mu_0 Z)\,\Phi_r(Z)$, where $u = 2\pi/\lambda$, we get

$$(18)\quad \frac{d^2\Phi_r}{dZ^2} - 2iu\mu_0\frac{d\Phi_r}{dZ} - \frac{4\pi^2r^2\cos^2\phi}{\lambda^{*2}}\Phi_r = -\frac{Bi}{2}\{\Phi_{r-1}e^{ibZ\sin\phi} - \Phi_{r+1}e^{-ibZ\sin\phi}\}$$

Putting $Z = (2\pi\mu)^{-1}\lambda\xi$ we obtain

$$(19)\quad \mu^2\frac{d^2\Phi_r}{d\xi^2} - 2i\mu_0\mu\frac{d\Phi_r}{d\xi} - \frac{r^2\lambda^2\cos^2\phi}{\lambda^{*2}}\Phi_r = -\mu_0\mu i\{\Phi_{r-1}e^{ia\xi\sin\phi} - \Phi_{r+1}e^{-ia\xi\sin\phi}\}$$

where $a = \lambda/\mu\lambda^*$

As μ is of the order 10^{-5} and μ_0 is of the order unity we may omit the first term and consider the equation

$$(20)\quad \boxed{2\frac{d\Phi_r}{d\xi} - (\Phi_{r-1}e^{ia\xi\sin\phi} - \Phi_{r+1}e^{-ia\xi\sin\phi}) = \frac{ir^2\lambda^2\cos^2\phi}{\mu_0\mu\lambda^{*2}}\Phi_r}$$

The relative intensity of the rth order is given by $|\Phi_r(\xi)|^2$. We may now show that, in general, $|\Phi_r(\xi)|^2 \neq |\Phi_{-r}(\xi)|^2$. We will prove the same by assuming the contradictory result. Suppose

$$(21)\quad \Phi_r(\xi) = e^{i\rho_r}\Phi_{-r}(\xi)$$

Then we get

$$(22)\quad 2\frac{d\Phi_{-r}}{d\xi} = (\Phi_{-r+1}e^{i(\rho_{r-1}-\rho_r)}e^{ia\xi\sin\phi} - \Phi_{-r-1}e^{i(\rho_{r+1}-\rho_r)}e^{-ia\xi\sin\phi}) = \left\{-2i\frac{d\rho_r}{d\xi} + \frac{ir^2\lambda^2\cos^2\phi}{\mu_0\mu\lambda^{*2}}\right\}\Phi_{-r}.$$

The actual equation for Φ_{-r} is

$$(23)\quad 2\frac{d\Phi_{-r}}{d\xi} - (\Phi_{-r-1}e^{ia\xi\sin\phi} - \Phi_{-r+1}e^{-ia\xi\sin\phi}) = \frac{ir^2\lambda^2\cos^2\phi}{\mu_0\mu\lambda^{*2}}\Phi_{-r}.$$

Comparing the equations, we obtain the result that they can never be identical unless $\phi = 0$ when $\rho_r = r\pi$. Thus in the case of oblique incidence in which $\phi \neq 0$.

$$(24)\quad \Phi_r(\xi) \neq e^{i\rho_r}\Phi_{-r}(\xi)$$

i.e., $|\Phi_r(\xi)|^2 \neq |\Phi_{-r}(\xi)|^2$.

This means that the intensity of the rth order is not equal to the intensity of the $-r$th order. Similar results corresponding to the above could be easily derived in the case of the standing sound waves on the same lines.

In case the coefficient of the term on the right-hand side of the equation (20) has no appreciable influence in the wave function and ϕ is small,

it can be shown that Φ_r approximates to the wave function given in Part II of this series of papers. In this case the diffraction pattern will be very nearly symmetrical.

4. Amplitude Changes on the Emerging Wave-Front of Light.

According to the notation of Part IV, the wave-function for a *general* periodic supersonic disturbance in the medium is given by

$$\psi = e^{2\pi i\nu t} \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{r,s}(z)\ e^{2\pi irx/\lambda *}\ e^{2\pi is\nu * t}$$

in the case of the normal incidence of the incident light to the sound waves. Therefore the intensity is given by

$$|\psi|^2 = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} A_{l,m}\ e^{2\pi ilx/\lambda *}\ e^{2\pi im\nu * t}$$

where

$$A_{l,m} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} f_{r,s}\, f_{r-l,\, s-m}\dagger.$$

† denoting the conjugate.

Thus, the intensity (or the amplitude) will be periodic in x and t on the wave-front which forms the basis of the explanation of the amplitude grating found by Bär[2] and Lucas.[6] This forms also the basis of the explanation of the observability of the sound waves found by the investigators[7] at Köln. In the case of a standing sound wave, *the average intensity with respect to time* will be given by

$$I(x, z) = \Sigma\, B_s\, B_s\dagger$$

where

$$B_s = \sum_{r=-\infty}^{\infty} f_{r,s}\ e^{2\pi irx/\lambda *}$$

and r *and* s *are both even integers or odd integers.* It follows from the above that $I(x, z)$ is periodic in $\lambda^*/2$.

The intensity (or the amplitude) will be constant on the wave-front when all $A_{l,m}$ vanish except $A_{0,0}$ as will be so in the case governed by the restrictions of Part I.

5. Summary.

The essential idea that the phenomenon of the diffraction of light by high frequency sound waves depends on the corrugated nature of the transmitted wave-front of light has been developed on general considerations in this paper to apply for the case of the oblique incidence of the incident light to the sound waves. It is found that the intensity distribution will not be symmetrical in general thus explaining the results of Debye and

Sears, Lucas and Biquard, Bär and Parthasarathy. The consideration of the amplitude changes of the traversing beam of light explains the results of Hiedemann, Bär and Lucas.

We are highly thankful to Prof. Dr. R. Bär of Zürich for having kindly sent us a copy of the proof of a paper by him describing experimental tests of our theory which is now in course of publication in the *Helvetica Physica Acta*.

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ELECTRONIC CONFIGURATION AND BOND ENERGY.

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Introduction.

Among the many band spectra of diatomic molecules known at the present time, if one excludes the permanent gases, those of the oxides have been easily the earliest to be observed. Lately, however, the number of band spectra of fluorides, chlorides, sulphides and of a few oxides which were still unobserved have been recorded and analysed by various authors. Even now the number of molecules whose spectra one would like to know is not large but a beginning can be made by a systematic survey and comparison of available data, to understand empirically the relationship between the bond energies determined by the spectra and the place of the constituent atoms in the periodic system on the one hand and the electronic configuration of the completed molecule on the other. In this paper we propose to start such an attempt. We shall not treat the hybrides because they approach closely the united atom and are a class by themselves. The oxides and halides of the second group and the oxides of the fifth group have been dealt with recently from a similar point of view[1] and these results will be bodily taken over for our present purpose.

Electronic Configuration and Dissociation Products.

(*a*) *Oxides of the third group.*—Since the halides of the alkali metals are electrovalent and the diatomic molecules formed by atoms of the second group are already dealt with, we start with the oxides of the third group. In addition to BO and AlO which have been known for some time we now know also GaO. Particular interest attaches itself to this because there exist two different theories on the connection between dissociation energy and electronic configuration, with which we shall deal presently below. The spectrum of BO has been discussed by Mulliken[2] from the view-point of his theory and that of AlO which is quite different from BO as far as dissociation energy is concerned, is discussed by Lessheim and Samuel[3] from the view-point of their theory. The spectrum of GaO is therefore

likely to bring about a decision on this question as far as the oxides of the third group are concerned.

In gallium oxide one band system[4] involving two $^2\Sigma$ terms is known for which the energy of excitation is 3.17 volts and the dissociation energies are 2.82 v. for the ground level X $^2\Sigma$ and 4.58 v. for the excited level B $^2\Sigma$. The energy difference of the products of dissociation is 4.93 v. (Fig. 1).

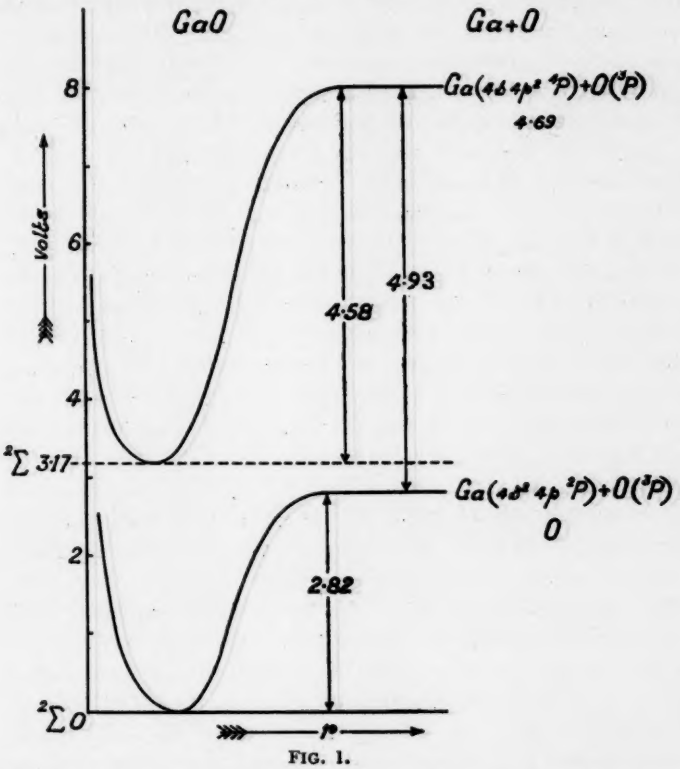

FIG. 1.

Exactly as in AlO, this constitutes a typical example of a molecule for which the dissociation energy increases on excitation.

The interpretation of such states of molecules really involves the essential difference between the two methods of treatment mentioned above. The method of molecular orbitals yields, as is well known, all the electronic configurations which give rise to the totality of electronic terms of a molecule. It is, however, not competent to distinguish the stable or attractive terms from the unstable or repulsive ones except by the introduction of

an additional hypothesis. One such hypothesis (Herzberg, Mulliken) is that the dissociation energy of a molecule is the resultant of the contributions of the single bonding and anti-bonding electrons; these are recognised as the non-premoted and premoted electron and the change of dissociation energy in the various states is attributed to the process of premotion. In the other view only those electrons contribute to the dissociation energy of a given level which, coming from different atoms, join to form pairs on the same molecular orbital. The essential difference between the two view-points therefore is that while for the first one the premotion has the first order effect and interaction between the electrons (other than that represented by a screening effect) only a subsidiary influence, exactly the reverse is true for the second method. On the basis of the latter view an increase in the dissociation energy of a molecule on excitation may then be due either to the removal of the odd electron, which represents a free valency as in BeF or NO, or to an increase in the number of electron pairs, giving rise to an increase in the number of chemical bonds, as for instance in BeO. The oxides of the third group are further examples of the latter case. Therefore in GaO as in AlO according to this interpretation we would expect that the term with an increased energy of dissociation is formed by the combination of unexcited oxygen with the Ga atom possessing two p-electrons, the s^2 group having undergone previous fissure. This is indeed borne out by experiment. The difference in the energy of the dissociation products is 4.93 volts and represents the energy of the transition $(4s^2\ 4p\ ^2P) - (4s\ 4p^2\ ^4P) = 4.69$ volts, which is indeed the lowest one of all those, which possess two p-electrons. There is, however, a term in which the s^2 group is intact, *i.e.* $(4s^2\ s\ ^2S)$ in Ga with an excitation energy of 4.64 volts. If this term is correlated to the upper level of the band system why other similar but lower terms like $(4s^2\ 5s\ ^2S)$ or $(4s^2\ 4d\ ^2D)$ are passed over in the process of formation of the GaO molecule, will be completely ununderstood. On the other hand, it is particularly significant that the strongest system of the GaO bands directly gives an empirical and straightforward correlation to the configuration of Ga with two p-electrons. From the configuration Ga $(4s^2\ 4p\ ^2P) + O$ $(2s^2\ 2p^4\ ^3P)$ many configurations for the molecule GaO are possible of which the following will have the lowest energy :—

$$s\sigma^2\,(s),\quad p\sigma^{*2}\,(s),\quad p\pi^4\,(p),\quad s\sigma\,(p)\qquad {}^2\Sigma$$

According to the above correlation the excited level is obtained by a combination of Ga, $(4s\ 4p^2\ ^4P)$ with O, (^3P). The energetically lowest possible configuration of this combination is :—

$$s\sigma^2\,(s),\quad p\sigma^*\,(s),\quad p\pi^4\,(p),\quad s\sigma^2\,(p),$$

the resulting term is indeed a $^2\Sigma$ in agreement with the experimental result. The increased energy of dissociation in the excited state is due to the formation of an additional bond. In the ground level, according to the conceptions of the pair-bond theory of linkage, (see below), only one bond is formed because, the *s*-electrons of Ga remain as a group by themselves in the GaO molecule and therefore do not take part in the linkage, and only the single *p*-electron joins with the electrons of O in a common molecular orbital. From a comparison of the two electronic configurations, it will be seen that the odd $s\sigma\,(p)$ electron belongs essentially to the O atom and that the single bond is formed in the $p\pi^4\,(p)$ group which is made up of three *p*-electrons of O and one of Ga. In the excited state this group remains intact. But the second *p*-electron of Ga, which is now available after the splitting of the s^2 group, joins the odd *p*-electron of O, completing the $s\sigma\,(p)$ group and thus giving rise to an additional bond.

These results are in complete harmony with those of AlO, where also the increase in dissociation energy in the excited state is brought about by an additional $p-p$ bond formed in exactly the same way. Thus among the three oxides of the third group whose spectra are known, two confirm the predictions of the pair-bond theory. The known spectra of BO alone indicate a different behaviour. The extrapolated dissociation energies correlate the lowest term of the BO molecule with excited terms of the separated atoms, and the excited terms of the normal atoms with the excited molecular state. Mulliken assumes that the extrapolated value for the lowest term of the molecule is too big and so makes it join the level of the unexcited atoms. If this is true, the term with an increased energy of dissociation, corresponding to that in GaO and AlO is not yet observed. Thus though BO does not support our explanation, it also does not contradict it. We are, however, inclined to believe that the X $^2\Sigma$ term of BO does not correspond to the ground level of GaO or AlO but to the excited level with increased energy of dissociation. From our experience about the extrapolated dissociation energy in a large number of similar molecules, we rather think that the reduction of 30% which is necessary for a correlation term of unexcited atoms is too much. The dissociation energy of this particular excited $^2\Sigma$ level has been found to be 4.6 volts in GaO and 6.2 volts in AlO, and therefore the extrapolated energy of 9.3 volts of X $^2\Sigma$, in BO, is about the correct order of magnitude.

(*b*) *Halides of the fourth group.*—Molecules possessing free valencies in the ground state are next met with among the halides of the fourth group. On account of the two *p*-electrons of the atoms of this group oxides and sulphides are stable molecules ; the diatomic halides, however, are, from the

standpoint of chemistry, only radicals. Like molecules of the type CaF or NO, these halides of the fourth group should therefore possess excited electronic terms which are more stable than their ground levels if the electron representing the free valency is partly removed by excitation to a higher group. Among the spectra of such molecules, indeed three cases are known in which this statement has been already confirmed. These are the molecules SiF, SiCl and SnCl. Among other molecules which have been mostly observed in absorption, the corresponding term with increased energy of dissociation has not yet been found. The molecule SnCl has been already discussed earlier[3,5] and it is shown that the combination of unexcited atoms in their configurations Sn ($5s^2\ 5p^2\ ^3P$) *plus* Cl (^2P) gives rise to a number of terms among which the ground state $^2\Pi$ with an energy of dissociation from 3.2 to 3.5 volts is one. The electronic configuration of the molecule in this state is :—

$$\sigma^2(s),\quad \sigma^{*2}(s),\quad \pi^4(p),\quad \sigma^2(p),\quad \pi^*(p)\qquad {}^2\Pi.$$

By an excitation of 4.2 volts we get to a $^2\Sigma$ state of the molecule for which the energy of dissociation is 4.8 volts and which is formed by the combination of unexcited Cl and excited Sn in the configuration ($5s^2\ 5p\ 5d$). The electronic configuration therefore is :—

$$\sigma^2(s),\quad \sigma^{*2}(s)\quad \pi^4(p),\quad \sigma^2(p),\ldots,\ \sigma(d)\qquad {}^2\Sigma.$$

From a comparison of the two atomic and the two molecular states it is evident that the predictions of the electron pair-bond theory are confirmed.

These conclusions are fully corroborated by two more molecules whose spectra have been recently analysed. The ground level of the molecule SiF ($^2\Pi$), has the following configuration[6] similar to that of SnCl :—

$$\sigma^2(s),\quad \sigma^{*2}(s),\quad \pi^4(p),\quad \sigma^2(p)\quad \pi^*(p),\qquad \mathrm{X}\ {}^2\Pi.$$

It is formed by the combination of unexcited atoms Si ($3s^2\ 3p^2\ ^3P$) + F (^2P), and has an energy of dissociation of 4.77 volts. Among the excited levels there exists a term B $^2\Sigma$ lying 4.29 volts above the ground level, having an increased energy of dissociation of 6.51 volts and the excitation energy of the products of dissociation (6.03 volts) correlates it to the level Si ($3s^2\ 3p\ 4p\ ^1S$) + F (^2P). Its electronic configuration is :—

$$\cdots\ \pi^4(p),\quad \sigma^2(p),\ \cdots,\ \sigma(p)\qquad \mathrm{B}\ {}^2\Sigma.$$

It will be seen that the configuration of the molecule in which the electron which does not contribute to the linkage is removed to a higher group, possesses an increased stability. Another excited term C $^2\Sigma$ for which the data are not very certain offers some evidence for a similar increase in stability if the non-binding electron of the Si atom is removed not to $4p$ as in the former case but to $4s$.

The data on SiCl are rather meagre and the constants are derived from but a few observations.[7] Only one band system is known which apparently belongs to the transition $^2\Sigma \rightarrow {}^2\Pi$, the latter being the ground state of the molecule. The extrapolated value 4.98 volts for the ground level is much higher than what one would expect from analogy with SiF which has 4.77 volts for its dissociation energy in the ground state. Similarly there is little doubt that the extrapolated value of 11.59 volts for the energy of dissociation of the $^2\Sigma$ level is abnormally too high leading to an excitation energy of 10.81 volts of the dissociation products, which is too low for the first excited term of F and above the ionisation potential of Si. It is however certain that the excited $^2\Sigma$ level has an increased energy of dissociation and dissociates into normal F and a highly excited Si atom in which one of the *p*-electrons must have been removed to higher orbits.

Dissociation Energy and Electronic Configuration.

The relation between the energy of dissociation and the electronic configuration of the molecule can be further followed throughout the periodic system. We shall compare firstly the bond energy in a class of compounds along one particular period such as, *e.g.*, the oxides of Mg, Al, Si, P, and S. This will enable us to trace the effect of the electronic configuration on the energy of the bond. Secondly, we shall follow the course of the dissociation energy along the different periods, comparing molecules such as the oxides of the fourth group, *e.g.*, CO, SiO, GeO, SnO, and PhO. This will give us the influence of the varying field strength and polarity on the energy of formation of the molecule.

In Table I we have collected the energies of dissociation in the ground state of a number of molecules. They are obtained mostly by linear extrapolation, except those of O_2 and S_2 which are obtained from the convergence limit of the absorption bands. These values do not all possess the same accuracy, the extrapolation being based in some cases on but a few vibrational levels, which are themselves obtained from only a few observations. In some cases the spectra have not been sufficiently investigated to give us the exact nature of the term and some of the data are from absorption bands alone. Especially the values in brackets appear to be much less reliable than the rest.

In the case of S_2 and CO things are not yet definite. Interpretations of rotational pre-dissociations observed in these molecules have been used to evaluate their energy of dissociation in the ground state.[8] But these interpretations have to face some objections. Rotational pre-dissociation will certainly give rather accurate values of the heat of dissociation but it

TABLE I.*

	Be	Mg	Ca	Sr	Ba
F	5·4	3·7	3·2	3·1	
Cl	4·3	3·9	3·5		
O	5·8	3·8	3·88	3·28	
	B	Al	Ga	In	Tl
F					
Cl	3·6	3·6	(2·0)	(3·1)	(2·3)
O	(~6)	4·2	2·8		
	C	Si	Ge	Sn	Pb
F		4·8			3·4
Cl		(5·0)		3·8	3·2
O	~10	7·8	7·3	5·8	4·3
	N	P	As	Sb	Bi
F				~4	3·6
Cl					3·0
O	6·7	6·5	5·0	5·3	
	O	S	Se	Te	
O	5·09	~5·1	4·2		

* For this and the following tables the constants of the molecules are taken from W. Jevons: "Report on Band Spectra" (London, 1932) and H. Sponer: "Molekuel Spektren (Berlin, 1936). For PbF G. D. Rochester: *Proc. R. Soc.*, 1936, **153**, 407; BiF, BiCl, etc. F. Morgan: *Phys. Rev.*, 1936, **49**, 41. For SiF R. K. Asundi and R. Samuel (Ref. 6); SbF from unpublished data.

has to be established unmistakably as for instance in the case of MgH. Otherwise it will be difficult to distinguish between true rotational predissociation for which a correlation to atomic levels is possible and the simple termination of band structure arising from rotational instability or from experimental conditions of excitation. In CO, for instance, the suggested interpretation is not compatible with Kronig's selection rule for multiplicity and the value of 8.41 volts for D (CO) leads to 107.9 K.cal./mol. for the heat of sublimation of carbon, a value which hardly can be reconciled with thermochemical data and particularly the behaviour of free radicals. In S_2 we have means of checking the interpretation of the abrupt termination of the rotational structure as genuine pre-dissociation. As we know,

the point of convergence in an absorption band spectrum is also one of the most accurate methods of deriving the energy of dissociation. Such a convergence limit for S_2 is found at $4.9 + 0.2$ volts.[9] If the dissociation products are normal atoms, this value is itself equal to D (S_2); or if we deduct once or twice the triplet separation of S (^3P), we obtain 0.07 or 0.14 volts less. On the other hand, if the products of dissociation involve a sulphur atom in the ^1D term, we obtain 3.8 ± 0.2 volts for D (S_2). None of these possible values agrees with 4.41 volts which is deduced from the interpretation of disappearance of rotational structure as true pre-dissociation. The wide discrepancy between the values on this interpretation and the data on convergence limit shows that the interpretations of pre-dissociation data are not always easy. For our present purpose therefore we take the values of ~ 10 volts of D (CO) and 3.8 volts for D (S_2).

In spite of these difficulties certain characteristic changes do exhibit themselves quite clearly and we proceed to point out and discuss them. If we compare the diatomic *halides*, we find that the dissociation energy

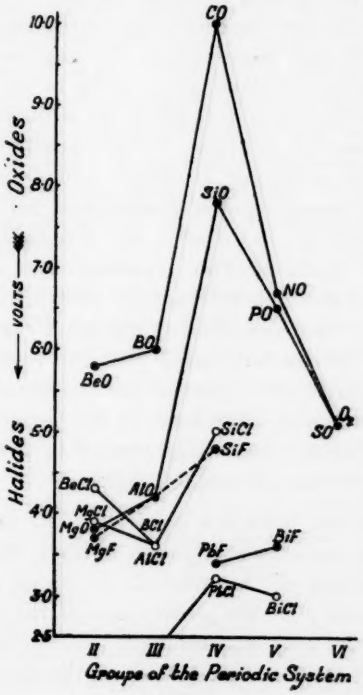

FIG. 2.

remains rather constant in the same period as will be seen also from the examples displayed in the diagram. There are slight differences, which indicate only a secondary superimposed effect. On the other hand, the energy appears to decrease from the second to the third group, but seems to rise again in the fourth group with a tendency to be rather constant later on. For example, BeCl has 4.3, BCl 3.6 volts showing the decrease from the second to the third group. AlCl with 3.6 and SiCl with something less than 5 volts indicate the increase from the third to the fourth group and so also do TlCl with 2.3 and PbCl with 3.2 volts. BiCl with 3.0 indicates a tendency for the dissociation energy to remain constant from the fourth to the fifth group.

We shall consider these tendencies from the view-point of the method of molecular orbitals. Firstly let us assume according to the original interpretation of this method, that each single electron contributes independently to the stability of the molecule as a bonding electron if it is not premoted, as an anti-bonding one, if it is premoted. From this standpoint, the ground levels of all the halides involve unexcited atoms. The outside *s*-electrons of the metal and the halogen form an unpremoted and a premoted σ^2 group, whose contributions to the bond cancel out and the linkage is produced by the *p*-electrons of the halogen atom alone in the earth alkali halides, and of the metal and the halogen both in the subsequent groups. Accordingly we get 5 unpremoted electrons in compounds like BeCl and 6 such electrons in BCl. The additional electrons in molecules of the subsequent types come now into non-premoted groups and SiF processes 6 bonding and 1 anti-bonding electron ($\pi^4\ \sigma^2\ \pi^*$), BiF 6 bonding and 2 anti-bonding electrons ($\pi^4\ \sigma^2\ \pi^{*2}$). Each electron represents half a positive or negative bond, as a consequence of which BeCl has $2\frac{1}{2}$, BCl 3, SiF $2\frac{1}{2}$ and BiF 2 bonds. This should show itself in an increase of the bond energy from BeCl to BCl, and a decrease from AlCl to SiCl, while just the reverse happens in each case. Here we have assumed, that all the *p*-electrons are on molecular orbitals. If it is presumed, that four of the *p*-electrons of the halogen remain on atomic orbitals, the disagreement is even more pronounced, because the percentage changes become bigger.

The other standpoint does not meet with any such difficulties. Here we obtain only a single bond in every case, because only such electron pairs contribute to the stability of the molecule in which electrons of both the atoms join, and because 4 of the *p*-electrons of the halogen atom form a π^4 group by themselves, only one electron joins in the same orbital with electrons of the metal atoms. The halides of the second group are formed according to this view by excited metal atoms with one *s*- and one *p*-electron,

for which experimental evidence seems to be convincing.[1] In BCl, SiF and BiF the metal atom possesses already a *p*-electron and is therefore capable of chemical union in its unexcited state. Thus we obtain everywhere the same type of a single *p*—*p* bond on which is superimposed the varying influence of the remaining electrons. An odd electron not contributing to the linkage may disturb and weaken it, but on the other hand, a hybridisation, *e.g.*, of the *s* and *p* functions as for instance in BeCl, may slightly strengthen the bond. Subject to such considerations this view-point certainly explains the course of the dissociation energy satisfactorily.

The superiority of this view-point becomes more evident from the following discussion of the *oxides*. In an oxide of the second group, according to the original interpretation of the method of molecular orbitals, again the two $\sigma^2(s)$ groups cancel out and the linkage rests on the four *p*-electron of oxygen alone, which are bonding electrons in the molecule. The ground state of the molecule being $^1\Sigma$ and that of O being ^3P, this interpretation has to assume, that it involves an oxygen atom already excited to ^1D. But also the combination of an unexcited metal atom of the second group with unexcited oxygen gives a bonding configuration with the same 4 unpremoted *p*-electrons of O and the resulting triplet term of the molecule should form either the ground level or at least a very low term in the electronic states of the molecules. But such a term has never been found. In any case oxygen having one electron less than a halogen, we obtain electronic configurations with one electron less than in the halides and accordingly 2 bonds in BeO, $2\frac{1}{2}$ in AlO, 3 in CO, $2\frac{1}{2}$ in NO, and 2 in O_2.

From the other view-point the known ground level $^1\Sigma$ of the earth alkali oxides is formed by neutral oxygen and a metal atom in the term $sp\ ^3P$. This has been corroborated by the correlation of the dissociation products of the higher electronic states of these molecules to atomic terms and particularly the occurrence of the anomalous terms of the metals leaves little doubt as to the justification of this correlation.[1] The molecules of the type of BeO possess therefore only a single bond in their ground state which has to be considered as a *p*—*p* or a hybridised *sp*—*p* bond. The oxides of atoms of the third group also possess only a single bond in their ground level, because only one *p*-electron is present in such unexcited metal atoms. The atoms of the fourth group are the first to possess two *p*-electrons in their unexcited state and therefore their oxides possess a double bond. The same holds for the atoms of the fifth and sixth groups, but their oxides possess one and two odd electrons respectively, which disturb and weaken the bond in the ground state.

Experimentally we find that the energy of dissociation remains constant or rather decreases from MgO and CaO to AlO and GaO.* From the discussion about BO, above, it is clear that the dissociation energy of unexcited BO is about 6 volts, whether the observed $^2\Sigma$ level is the ground level or not. This value is again identical with that of BeO and considerably less than that of CO. If we compare the oxides of the atoms of the fourth group with the corresponding oxides of the second and third group, we get the interesting result, that the energy of dissociation shows a big increase and is about doubled. In the next groups, molecules of the NO and SO types, the dissociation energy is again decreased in two distinct steps.

The decrease of energy as we go from the fourth group to the sixth finds its explanation equally well from both the above view-points, from the assumption of premotion in the one case, and from that of the disturbing effect of the odd electrons in the other. On the other hand, the observed change from the second group to the third and fourth groups, can only be explained by the second view-point. From the first view-point a regular increase would be expected, so that the oxide of the atoms of the third group would have a dissociation energy midway between the oxides of those of the second and fourth. But, as the discussion in the first section of this paper has shown, BO, AlO, and GaO possess about the same dissociation energy as the corresponding oxides BeO, MgO and CaO, and one half to two thirds of that of CO, SiO, and GeO. From the second view-point such a course of the dissociation energy is just what one would expect. So long as a single bond persists as it does in the oxides of the second and the third groups, the dissociation energy is roughly of the same order of magnitude; as soon, however, as we reach the fourth group where the pure double bond manifests itself without the presence of disturbing electrons, the dissociation energy suddenly increases to nearly double the value. This to our mind indicates another evidence in favour of an interpretation of the method of molecular orbitals as an electron pair-bond theory of valency.

We shall now follow the course of the dissociation energy along different periods, comparing for instance the oxides and sulphides of the fourth group with each other, the spectra of these molecules being known better than of those in any other period. It can be seen from Table II that the energy of dissociation decreases as we proceed along a row or go down along a column. This means that the bond energy runs parallel to the field strength, with no regard to the polarity of the molecule. From CO to PbO

* The departure of GaO from CaO is much more pronounced than that of AlO from MgO, but we believe that the value of CaO is slightly too high because it cannot be higher than that of MgO.

TABLE II.

	C	Si	Ge	Sn	Pb
O	~10	7·8	7·3	5·8	4·3
S	7·8		5·7	5·5	4·7
Se	4·2				

the bond energy decreases, whereas the polarity increases, while from CO to CSe both decrease together. It has been pointed out already elsewhere[10] that such a course is not compatible with a theory in which each single electron contributes independently towards the energy of formation. In such a theory the wavemechanical interaction of the electrons (other than that represented by a simple screening effect), is neglected and the bonding effect is due to the degeneracy of the nuclear fields. But the polarity is another expression for the dissymmetry of the nuclear fields and this theory should predict the bond energy and the polarity to run together. That is another instance again in favour of the electron pair-bond theory of valency.

The difference between the two interpretations of the method of molecular orbitals shows itself in polyatomic molecules as the difference of non-localised and localised bonds. With the exception probably of hydrides and certainly of aromatic compounds, where non-localised electrons are present, brought about by hybridisation of the localised bonds, and where they just produce the specific aromatic character, the pair-bond theory of valency leads to localised bonds as a result of the wavemechanical interaction, mentioned above, while its neglection leads to non-localised bonds, and this neglection is necessary if the energy of formation of a molecule shall be conceived as the sum of the contributions of individual independent electrons. We have shown elsewhere,[11] that a close correspondence exists among the ω values known from infra-red and Raman spectra of certain polyatomic molecules and those of the constituent diatomic radicals, known from band spectra. Though the number of such instances known is not very large at the present moment, we believe that the coincidences are not fortuitous and that they therefore favour the conception of localised bonds. We have further tried to follow this correspondence in respect of dissociation energies. In the case of the chlorides and oxychlorides of di- and tetravalent sulphur a correlation between the bond energies could be established by their photodissociation[12] and it was found, that, *e.g.*, the S = S bond has the same energy in polyatomic molecules as is obtained from the band spectrum of S_2. An

extension of such a correlation to other molecules is not so conclusively possible for want of sufficient and reliable data. In spite of this we should like to point out certain interesting features among the available instances. The values of dissociation energy obtained from the usual linear extrapolation of vibrational levels are by no means satisfactory in many cases, if taken individually. But there seems to be little doubt that the errors thus introduced cancel out, probably because they are in the same direction, when we correlate the products of dissociation in different electronic states of one and the same molecule to the terms of the constituent atoms. For our present purpose we shall have to use individual values which therefore are not absolutely correct and therefore are expected to differ from the thermochemical values.

Among the few instances, which are available for such a comparison there are some, which exhibit a close relation between the bond energies of the diatomic radical molecule and the saturated chemical molecule. Denoting by D_0 values from the dissociation energy derived from band spectra and by D_T such from thermochemical measurements (both in volts), we collect them in the following table :—

TABLE III.

	D_0	D_T	D_T'
AgO	1·8	1/2 D_T (Ag_2O) = 1·9	
PbCl	3·3	1/2 D_T ($PbCl_2$) = 3·4	1/4 D_T ($PbCl_4$) = 2·1
BiCl	3·6	1/3 D_T ($BiCl_3$) = 3·3	
BiBr	2·7	1/3 D_T ($BiBr_3$) = 2·4	
SbF*	~4	1/3 D_T (SbF_3) = 4·6 (5·6)	
SO	5·1	1/2 D_T (SO_2) = 5·4	1/3 D_T (SO_3) = 4·7
SeO	4·2	1/2 D_T (SeO_2) = 4·5	1/3 D_T (SeO_3) = 3·7

* For the thermochemical energy of formation two values exist in literature, which lead to 4.6 and 5.6 volts, respectively (*cf.* Mellor).

It is interesting to note, that where a comparison is possible, D_0 agrees better with the thermochemical value derived from the molecule with lower valency than from that with maximal valency of the central atom. The best known example for such a behaviour is of course CO, where D_T (CO)

gives 235 K.cal./mol., $\frac{1}{2}$ D (CO_2) 181 K.cal./mol. This is connected with the fact, that the D_T values for such molecules with maximal valency are not bond energies at all, *i.e.*, do not refer to the *adiabatic* dissociation by excitation of the vibrational levels, because the ground level of a molecule like CO_2 or SO_3 is not formed by the combination of unexcited CO or SO_2 and unexcited O atom. This is clear from the diamagnetic character of these molecules and absorption spectra indicate, that the halides of the maximal and minor state of values are in a similar relation[12] at least from the fourth group of the periodic system onwards. It cannot be said for certain whether the ground level of a molecule like SO_3 involves excited oxygen atoms or excited SO_2 molecules, but since the pair-bond view would be better satisfied by the splitting off of the original s^2 group of S, the above relation appears again to favour the latter standpoint.

It is further interesting to note, that in cases like AsO and SbO the values $\frac{1}{3} D_T (As_2O_3) = 7.6$ and $\frac{1}{3} D_T (Sb_2O_3) = 7.3$ volts agree better with the dissociation energy of those terms of AsO and SbO in which the odd electron is already partly removed. The dissociation energy of the ground level of AsO is 5.0, that of the $B\,^2\Sigma$ term is 6.1 ; the corresponding figures for SbO are 5.3 and 6.2 volts. The energies of formation of N_2O_3 and P_2O_3 are not certain, but we may expect the same relation there also.

Conclusions.

The original interpretation of the method of molecular orbitals as a theory of valency, in which the single electron possesses bonding power was based on the assumption that non-premoted electrons are bonding and premoted ones are anti-bonding or non-bonding. This assumption is not the outcome of any requirements of theory but is an empirical postulate, which seeks justification in experimental facts. Earlier attempts at correlation between the electronic levels of molecules and the energy states of the constituent atoms indeed appeared to lend support to this assumption. Later investigations have, however, shown that completely different correlations are possible and are absolutely necessary to satisfy the experimental facts. For example, in a molecule like BeO the stable triplet term, which should arise from unexcited atoms according to the older correlation, is not found and by the correlation of certain excited terms to anomalous terms of the metal atom it is shown, that a non-premoted odd electron in the configuration of the ground level lowers its dissociation energy. Similar remarks apply to the types BeF and NO and the new correlation of molecular terms to atomic states from the pair-bond view is shown to be satisfactory without exception in a larger number of molecules of these three classes, recently.

These three types represent molecules with free valencies and indeed just in such molecules the difference of the two view-points must become apparent. For other such molecules with free valencies, whose band spectrum is investigated in detail, *i.e.*, for the oxides of the third and the halides of the fourth group of the periodic system, only one example of each, *i.e.*, AlO and SnCl, was originally available. We have now shown in the present paper, that the correlation according to the pair-bond theory of valency holds also for other molecules of this type and appears to be generally valid. *All this evidence*, concerning the band spectra of oxides and halides of the second, third, fourth, and fifth groups of the periodic system *is definitely against the postulate of the identification of premoted and non-premoted with non-bonding and bonding electrons*. On the other hand, such a satisfactory correlation from the pair-bond view necessitates a revision of the theory of valency, based on the results of band spectroscopy.

From the purely experimental point of view an interpretation of the method of molecular orbitals as electron pair-bond theory of valency is furthermore supported by the course of the bond energies in the periodic system. The near relationship shown at the present moment in a few instances, between the bond energies of diatomic radical molecules with those of polyatomic chemical molecules, in which however the maximal valency does not manifest itself, also points in this direction. The close correspondence between the ω values of polyatomic molecules and of their radicals in the ground state in many cases and in the excited states also of some polyatomic molecules whose spectra have been recently investigated,[11] indicate a localisation of bonds which is the direct outcome of the pair-bond theory of valency. Further evidence in favour of this view is afforded by absorption spectra and photo-dissociation of halides and oxyhalides of di- and tetravalent sulphur, selenium, and tellurium, all of which show almost a rigorous constancy of each bond energy. To our mind, therefore, all this spectroscopical evidence undoubtedly bears out the electron pair-bond theory of valency.

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ULTRASONIC VELOCITIES IN ORGANIC LIQUIDS.

Part III. Esters and Ethers.

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1. Introduction.

In Part I[1] of the series, the ultrasonic velocities in several organic liquids were given and their relationship to chemical constitution was pointed out. In Part II[2] the velocities in several di-esters were determined, and the effect of lengthening of the chain, of methyl and ethyl radicals and several other features not reported earlier were discussed. The present paper forms a continuation of the series, the investigation being mainly confined to esters (mono-) and ethers.

The determination of the ultrasonic velocity was made by the diffraction of light by high frequency sound waves and the experimental details of arrangement and set-up were given in the first paper. The arrangement was the same as before.

Pure liquids were used after distillation.

The frequency of vibration employed was 7.382×10^6 c/s, but it was also checked every now and then, being corrected if there was any change.

The temperature noted against each liquid is that of the liquid itself, measured just at the time of taking the diffraction spectra.

2. Results.

Table I (given on page 483) gives ultrasonic velocities in some ethers and esters, and also adiabatic compressibilities calculated from such velocities.

No determination of velocity of sound seems to have been made for any of these compounds.

Even data of adiabatic compressibilities are few and below (Table II) is given a comparative table for such of those as are known so far. They are taken from a paper by H. Shiba.[3]

TABLE I. *Ultrasonic velocities in organic liquids at* 7.382×10^6 *c/s.*

	Liquids	Chemical Formula	Temp. in °C.	Velocity of sound in meters/second	Adiabatic compressibility $\beta\phi \times 10^6$
	A. ETHERS:				
1	Resorcin monomethyl ether	$C_6H_4(OH)(OCH_3)$	26·0	1629	32·9
2	Resorcin dimethyl ether	$C_6H_4(OCH_3)_2$	26·0	1460	44·5
3	O-cresol methyl ether	$C_6H_4(CH_3)(OCH_3)$	26·5	1385	53·0
4	*m*-cresol methyl ether	$C_6H_4(CH_3)(OCH_3)$	26·0	1385	53·4
5	O-cresol ethyl ether	$C_6H_4(CH_3)(OC_2H_5)$	25·0	1315	61·2
6	Anisol	$C_6H_5 \cdot O \cdot CH_3$	26·0	1453	48·0
7	Phenetole	$C_6H_5 \cdot O \cdot C_2H_5$	25·5	1361	56·1
8	Amyl ether (iso)	$C_5H_{11} \cdot O \cdot C_5H_{11}$	26·0	1153	97·2
	B. ESTERS.				
9	Propyl acetate (*n*)	$CH_3 \cdot COOC_3H_7$	26·0	1182	80·3
10	Butyl acetate (*n*)	$CH_3 \cdot COOC_4H_9$	26·0	1179	82·6
11	Amyl acetate (iso)	$CH_3 \cdot COO \cdot C_5H_{11}$	26·0	1168	83·8
12	Amyl formate	$H \cdot COO \cdot C_5H_{11}$	26·0	1201	79·8
13	Methyl chloracetate	$CH_2Cl \cdot COOCH_3$	26·0	1331	45·8
14	Ethyl monochloracetate	$CH_2Cl \cdot COOC_2H_5$	25·5	1234	56·6
15	Ethyl acetoacetate	$CH_3 \cdot CO \cdot CH_2 \cdot COOC_2H_5$	25·5	1417	48·8
16	α-Picoline*	$C_6H_4N \cdot CH_3$	28	1453	49·9

TABLE II. *Comparison of values for adiabatic compressibilities.*

Liquids	Shiba		Author	
	$\beta\phi \times 10^6$	T°	$\beta\phi \times 10^6$	T°
Propyl acetate (*n*)	85·2	25°	80·3	26
Butyl acetate (*n*)	82·6	25°	82·6	26
Amyl acetate (iso)	82·4	25°	83·8	26

* By an oversight the velocity of sound in α-picoline was given in Part I, exactly 2/3 the value it should have; the corrected value is 1491 m/s at 24°. The velocity given here is as 28°C. and the agreement is good, if allowance is made for the temperature coefficient of velocity.

Except for propyl acetate, for which Shiba's value is a little high, the agreement in the two sets of values for $\beta\phi$ is good.

3. Discussion.

Determination of ultrasonic velocities in related compounds of ethers and esters makes it possible to discuss the relationship between sound velocities and chemical constitution. The ground was covered in a general way in Part I. We shall examine the ethers and esters more closely in this paper, from the results given here.

A. Ethers.

Resorcin ethers.—The monomethyl ether shows higher sound velocity than the dimethyl ether. This is mostly due to the influence of (OH) group in the monomethyl ether, which gives it greater electric moment.

Cresol methyl ethers.—In the toluidines and the xylenes, the sound velocity in the ortho-compound was found to be appreciably higher than that for the meta- or the para-compound. In the two ethers, cresol methyl ethers, however no such difference could be noticed.

Methyl and ethyl ethers.—Data are available here to compare the two ortho-ethers, (*a*) O-cresol methyl ether and (*b*) O-cresol ethyl ether. The methyl ether has a decidedly higher velocity, even allowing for the small difference in their temperatures at which they were investigated. Such an increase in the velocity for a methyl compound was noticed for esters, the methyl ester showing always higher velocity than the ethyl ester of the same acid. Here we have an analogous case, for the methoxy radical behaves in a similar way. In both the types of compounds two carbon atoms are linked through an oxygen atom.

Anisol and phenetole.—Anisol is the phenyl methyl ether, while the corresponding ethyl ether is phenetole. The same argument of the methoxy group giving greater sound velocity applies also here. The behaviour of esters and ethers is different from other compounds in this respect, that though ethyl radical increases the chain in length, gives, in fact, less sound velocity than the methyl compound.

Aliphatic and aromatic ethers.—The sound velocity for anyl ether has been redetermined under the same conditions, and gives, if allowance is made for the temperature correction, good agreement with the value previously determined. A review of all the data on aliphatic and aromatic ethers makes one surmise that the sound velocities in the aromatic series are, in general, higher. Such a view was also expressed with regard to the hydrocarbons, and other substituted compounds. It is extended to the class of ethers.

B. Esters.

Acetates.—The three acetates, prophyl, butyl and anyl acetates have been experimented on for sound velocity at the same temperature, namely 26° C. As before, we find that with increase in the length of the alcohol radical, the sound velocity decreases markedly, at least the difference between the first and the last member is noticeable. This follows from the general conditions in Parts I and II.

Anyl esters.—It has been observed before, that even by lengthening the acid radical, instead of the alcohol, lowers appreciably the sound velocity for even two successive members of any series. As examples we took before, the ethyl esters of formic, acetic, propionic and butyric acids and showed that the sound velocity decreased from member to member, in spite of the increase in the length of the chain. Even so, here, anyl formate has higher sound velocity than anyl acetate.

Chloracetates.—The sound velocity in methyl chloracetate is 1331 meters/second at 26° C. and that in ethyl chloracetate is only 1234 meters/second at 25°·5 C. This is not surprising in view of what has been repeatedly said, on the effect of substitution of a methyl radical in place of ethyl, in esters.

Acetates and Chloracetates.—It was remarked in Paper I that substitution of a heavy atom generally lowered the sound velocity, as for example in the series, methylene chloride, chloroform and carbon-tetrachloride. However, we find that a similar substitution of a heavy atom in the esters, results in enhancing the velocity. This is borne out in the following Table.

TABLE III.

Ester	Sound velocity in m/s	T °C.
Methyl acetate	1211	24
Methyl chloracetate	1331	26
Ethyl acetate	1187	23·5
Ethyl chloracetate	1234	25·5

Ethyl acetoacetate.—The sound velocity in this compound is rather high for a mono-ester, especially for a long chain molecule like this one. However, since there is a ketonic group, and as we have noticed already in

ketones, as in other classes than ethers and esters, lengthening of the chain indicates higher sound velocity, we can attribute this higher velocity to the presence of the ketonic group.

The author's best thanks are due to Sir C. V. Raman for his interest in the work.

Summary.

Ultrasonic velocities have been determined for a number of ethers and esters. They are correlated to chemical constitution and in general we may conclude (*a*) *that for ethers* (1) methyl and methoxy groups seem to favour greater sound velocity compared to ethyl and ethoxy groups, and (2) aromatic ethers show higher velocities than those of the aliphatic series; and (*b*) *that for esters* (1) heavier acid or alcohol radical lowers sound velocity in spite of lengthening of the chain, and (2) the introduction of a heavy atom like chlorine in the acid radical enhances the velocity, as against diminution in velocity observed in the series methylene chloride, chloroform and carbon-tetrachloride. Some points of similarity between ethers and esters, with regard to the sound velocity, are pointed out.

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ON THE ABSORPTION SPECTRA AND LINKAGE OF INORGANIC NITRATES AND SULPHATES IN THE VAPOUR STATE.

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Introduction.[1]

Experiments of Franck and his collaborators[2] have shown that absorption spectra of diatomic salts in the vapour state are well qualified to distinguish between covalent and electrovalent linkage in such molecules.* Whereas alkali halides are electrovalent in the vapour state, as one would expect, halides of the first sub-group of the periodic table, like those of silver, were found to possess a covalent bond and furnished for the first time a clear example, that a particular bond may change its character and be either covalent or electrovalent in the same molecule according to the experimental conditions. This result, at the first moment surprising, is naturally of great interest for any physical understanding of chemical linkage and made it desirable to extend such investigations to polyatomic molecules.

The criterion by which Franck was able to distinguish between atomic and ionic binding, was that the term of a molecule which originates in two neutral and unexcited atoms, naturally is the ground level of a covalent molecule but forms an excited term of an electrovalent one, because here the ground level is formed by a combination of two ions. This criterion cannot be used in the case of polyatomic molecules. Firstly, it is known on

* A bond is termed 'covalent' here if the molecule dissociates into neutral atoms by adiabatic excitation of the vibrational levels of its ground state, and 'electrovalent' if this adiabatic dissociation produces ions. We thus identify the chemical terminology with that of Franck (atomic molecules and ionic molecules), but it should be clearly understood, that we speak of the character of the bond of a molecule only under well-defined experimental condition. It will be seen, that a bond, *e.g.*, that between potassium and oxygen in KNO_3, may be covalent in the vapour state and electrovalent in solution on account of the additional energy of hydration. Only with this proviso it is permissible to identify the chemical terminology with the above definition without confusion. A covalent bond may be polarised or not and the molecule possessing a dipole moment or not will be termed a polar, a non-polar molecule respectively, according to the terminology, introduced by Debye.

account of later investigations, that this criterion is not rigorously valid, partly because the combination of two atoms in particular states may give rise to a large number of attractive and repulsive terms, and partly because inter-sections of the potential curves of the electronic terms among themselves are quite possible. The chlorides and oxychlorides formed by atoms of the sixth group are examples of the first type.[3] According to their absorption spectra they dissociate in their region of selective absorption with lowest energy into normal atoms, but chemical and physico-chemical evidence (like conductivity, Raman effect, etc.) show, that they still possess a covalent bond in the liquid state and in solutions and we have to conclude *a fortiori* that they will possess a covalent bond in the vapour state, because even the additional energies of hydration or association, produced by the dipole moments of the surrounding molecules, have not been strong enough to turn the covalent bond into an electrovalent one. In some cases the Raman effect is observed directly in the gaseous state and according to Placzek's theory,[4] the Raman effect, depending on the change of polarisation with the internuclear distance, is a criterion of covalent linkage. The results of absorption spectroscopy of polyatomic molecules are, however, not surprising, since the number of repulsive terms increases rapidly with the number of constituent atoms and the excitation of an electron by illumination apparently means the transition from the ground level of the molecule to an excited repulsive term, both together possessing the same level of unexcited atoms as that of the dissociation products. This is equivalent to an intersection of the two potential curves at large internuclear distance and may be taken as a special case of the second possibility, mentioned above. The dissociation of the ground level of a covalent molecule into excited atoms and that of an excited molecular term into unexcited atoms owing to the intersection of two curves of the Franck-Condon diagram at small internuclear distance appear to be realised in a case like CaO. Photodissociation into unexcited atoms obtains according to the continuous absorption spectrum,[5] whereas the band spectrum indicates a covalent molecule in the vapour state and no perturbations have been found, warranting an explanation on the assumption of an hybridisation of the ionic and the atomic potential curve. It has been shown[6] that the ground level of such molecules does not arise from that of the two unexcited atoms but involves an excited metal atom in the state $sp\ ^3P$. The metal atom in its normal state ^1S, the electrons forming a closed group, s^2, gives rise to a repulsive curve which intersects that of the ground state of the molecule. Apparently this repulsive level which involves unexcited atoms forms the final state of the photolytic process. Experimentally the repulsive character of the

s^2 configuration has been definitely confirmed by the band spectrum of CdF, where the discrepancy between the energies of excitation of the dissociation products and the energy differences between the excited terms and the ground state of Cd is too large to be explained by an inaccuracy of the Birge-Sponer method of linear extrapolation.[7]

Besides these theoretical considerations also practical reasons do not permit the application of Franck's criterion to polyatomic salts. The fact, that the first photodissociation produces unexcited atoms in the alkali salts, was established by the agreement of the energy difference of the various regions of selective absorption with those of the atoms concerned. This procedure is not possible for polyatomic salts, because the electronic levels of the ions or radicals such as NO_3^- or the $-O-NO_2$ group are not known. We have therefore taken absorption spectra of some polyatomic inorganic salts where it is possible to distinguish empirically between the spectrum of the covalent and the electrovalent form. Thus the spectrum of inorganic nitrates in solution is known along with that of HNO_3 and ethyl nitrate in the vapour state, that of potassium sulphate in solution along with dimethyl sulphate and diethyl sulphate in substance and in solution of ether and that of the nitrite ion is known as well as that of ethyl nitrite in the vapour state. In all these cases the absorption spectrum of the covalent form, *e.g.*, of the organic ester differs from that of the free ion in dilute aqueous solution and allows us to distinguish the electrovalent form from it. Details will be discussed below. Such compounds like nitrates appear to be suitable also because their decomposition on heating invariably liberates rather large quantities of NO_2, which can be recognised easily by its two characteristic sets of bands the first being at about 6000 to 3500 A.U., and the second one from about 2400 A.U., onwards. It can be assumed, that the measured absorption spectra really correspond to that of the non-decomposed substance as long as these bands do not appear on the plates. The same bands served as an indicator of decomposition for potassium nitrite and those of SO_2 at about 3000 A.U., and 2200 A.U., in the case of the sulphates. It will be seen that among the nitrates those of the alkali metals stand heating better than silver nitrate, and among the divalent nitrates $Cd(NO_3)_2$ decomposes very rapidly, $Pb(NO_3)_2$ and still more $Mg(NO_3)_2$ can be heated to higher temperatures. Again Ag_2SO_4 decomposes much more rapidly than K_2SO_4 and our impression according to these few experiments is, that decomposition on heating obtains the earlier, the higher the ionisation potential of the metal atom or, what is the same, the more the molecule becomes non-polar and the more it approaches the true homopolar type of binding. On the other hand, the stability of

more complex molecules is naturally decreased very much and ammonium salts decompose at comparatively low temperatures. It was possible to study the absorption spectrum of ammonium nitrate but the decomposition of ammonium sulphate was so rapid and the amount of SO_2 liberated at low temperatures so great, that its spectrum could not be investigated.

Absorption Spectra of Related Substances and of Salts in Solution.

The absorption spectrum of the nitrate ion has been investigated by a number of authors and is very well known indeed, so much so that it is sometimes recommended for calibration purposes.[8] According to qualitative measurements of Hartley and K. Schæfer[9] the spectrum of nitric acid in diluted solutions in concentrations from $0.2\,m$ to about $10\,m$ exhibits a maximum in the region of $300\,m\mu$. Such a maximum is also characteristic for the nitrates of the alkali and earth alkali metals in solution. The maximum disappears gradually, with higher concentrations of the acid, up to $23.12\,m$ (98.6% acid), it flattens out more and more, until a continuous end—absorption remains with a point of inflection in the region between 263 and about $273\,m\mu$. Schæfer and Hantzsch[10] ascribed the maximum of selective absorption at $300\,m\mu$ in very diluted aqueous solutions to the nitrate ion, the end-absorption with the superimposed flat maximum at about $265\,m\mu$ of the highly concentrated solutions to a covalent molecule H–O–NO_2.

Quantitative measurements of the absorption curve of nitrates and nitric acid in various solvents by v. Halban[11] and Scheibe[12] have confirmed this point of view. Mention may be made of the spectrum of nitric acid in hexane and of ethyl nitrate in the liquid state and in solution which show again a diffuse maximum at about $272\,m\mu$ where as the distinct maximum of inorganic nitrates in solutions of low concentrations lies at $302\,m\mu$. Finally the absorption curve of ethyl nitrate in the vapour state was measured quantitatively by J. W. Goodeve,[13] who obtained again a point of inflection between $278\,m\mu$ and $244\,m\mu$. There is no doubt that these measurements establish a spectroscopical criterion which enables us to distinguish between the true electrovalent and the true covalent bond in this particular case. The former one, *i.e.*, the free nitrate *ion* exhibits a maximum of selective absorption at $302\,m\mu$, but whenever the linkage between the NO_3 group and the positive partner of the molecule is due to atomic binding and not to electrostatic forces between ions, this maximum disappears and is replaced by a very diffuse one, whose highest point is difficult to measure and sometimes not at all, but which lies approximately between 263 and $275\,m\mu$.

This interpretation of the spectrum in solutions of very low and very high concentrations is generally accepted, but that of solutions of nitrates

and nitric acid of medium strength, up to about 10 *m*, is more difficult. The spectrum of diluted solution of nitric acid and that of inorganic nitrates in highly concentrated solutions and in the presence of foreign ions still show a distinct maximum in the region of 300 $m\mu$, but its wave-length and intensity varies from that of the undisturbed nitrate ion. Similar phenomena obtain for aqueous solutions of the acid of medium concentrations and for diluted solutions of HNO_3 in other acids like $HClO_4$ a.o. Also KNO_3 in highly concentrated solutions of H_2SO_4 (80 to 95% in the presence of SO_3) shows the characteristic curve of the acid. Sometimes, particularly in solution in ether, the point of inflection (what we called the diffuse maximum) due to the covalent H–O–NO_2 molecule develops to a slightly more distinct maximum at 265 $m\mu$ and the same is true for solution in highly concentrated $HClO_4$.

Hantzsch and Schæfer tried to account for all these phenomena by various equilibria between the electrovalent form $O_2NO^- + H^+$ and the covalent form O_2NOH. They assumed a high percentage of covalent molecules not only in strongly concentrated aqueous solutions of nitric acid ($c = 10\,m$ and more) but also in solutions of medium strength (between 1 and 10 *m*). Halban and his collaborators contradicted this interpretation for concentrations of medium strength on account of their new measurements carried out under various conditions. They showed, that a high percentage of covalent molecules in solutions up to 10 *m* does not agree with other physico-chemical measurements (such as conductivity, partial pressure, etc.) and assumed for the explanation of the various observed optical effects a third form of nitric acid between the covalent and the electrovalent one.

Solutions of strong electrolytes at high concentrations, *i.e.*, in that region in which the theory of Debye-Hueckel does not hold any longer, possess a more complicated structure than was originally assumed. Much of the above controversy was doubtless due to the fact, that some years ago the knowledge of the condition prevailing in such highly concentrated solutions was even less than what it is to-day. Recent investigations of Scheibe[12] and von Halban and his collaborators[11] themselves on the absorption spectra of organic and inorganic molecules under various conditions and some work on complex salts carried out in this laboratory on similar lines[14] have shown that quite different effects obtain, qualified to change the absorption spectrum quite considerably in highly concentrated solutions or in the presence of foreign ions. We have at least to distinguish the effects of dehydration, of deformation and of a change of the probability of transition (of the amplitude of the classical dispersion formula) alone resulting from various degrees and kinds of polarisation owing to the interaction of the absorbing ion with other ions or the dipole molecules of the solvent. The probable

change of the absorption curve of cations and anions on account of these effects has been tentatively discussed by several authors,[14] and, for the present purpose it is sufficient to say, that these effects may produce a considerable change of the potential curves of the electronic terms and hence of the absorption spectrum. All these effects are finally due to various kinds of polarisation of the absorbing molecule and we have to conclude that the absorption spectrum of a particular molecule is not a fixed and determined quantity but depends on the state of polarisation. If this is true, some of the arguments of von Halban and collaborators do not appear to be so strong as was originally believed. If the varying polarisation of a molecule has to be considered, it is not essential, whether the absorption curve shows a point of inflection only or a slight genuine maximum at about the same wave-length. What is essential is, that the curve is not monotonous ; but whether or not a diffuse or distinct maximum is developed depends on the probabilities of transition and hence on polarisability and polarisation. It is not essential, whether a maximum has been found at exactly the same wave-length under various conditions or not, since this depends on the relative position of the two potential curves concerned, which itself depends on the polarisation. Also the construction of the absorption curve of a mixture of two absorbing kinds of molecules from those of their pure solutions cannot give accurate results nor can we expect all the curves of two kinds of absorbing molecules being in equilibrium, to intersect accurately at the same wavelength,[15] because Beer's law is not rigorously true, whenever the absorption depends on the polarisation as a further parameter, and therefore, *e.g.*, on the concentration.

On the other hand it is quite evident that the change observed in solutions of nitric acid of a concentration up to about 10 *m* cannot be even approximately explained by assuming high percentage of covalent molecules $H–O–NO_2$. Furthermore, Hantzsch explains certain deviations by formulating the electrovalent form in solution as $[NO_3]^-\ [H_3O]^+$ and similarly assumes the presence of isomeric forms of the type $[ON\ (OH)_2]^+ + [NO_3]^-$ or $[ON\ (OH)_2]^+ + [ClO_4]^-$ in homogeneous nitric acid (in the absence of water) and in mixtures with other acids respectively. It is quite true that the hydrogen ion forms particularly stable products in association with water or any other dipole molecule, because the proton having no dimensions in the ordinary sense is able to approach closer to the centre of negative polarity and its distance from the nucleus of the oxygen atom may even be smaller than that of its own outside electrons, and such association products may even be present in mixed crystals or solid solutions ; but it remains doubtful whether such formulations serve a useful purpose. They conceive such

associations as a new class of molecular formations as distinct from other products of association or hydration, whereas in reality the physical nature of the binding force is the same in the former and in the latter ones and there is only a difference of degrees not of quality between them.

Some of the differences of opinion on the structure of such solutions are, however, due simply to different points of view and therefore of terminology. Most physicists, for instance, will consider the transition from covalent to electrovalent linkage as an effect of first order ; the greatest interest is then attached to the fact that the two limiting cases of very highly diluted and very highly concentrated solutions can be distinguished by the absorption curves of the nitrate ion and the covalent molecule $H–O–NO_2$. The various optical effects in concentrations of medium strength are superimposed effects of second order owing to the various kinds and degrees of polarisation. The absorption curve of any concentration is considered to be due to an equilibrium of these two forms alone. For the effects in solutions of medium strength not the presence of a high percentage of the covalent form is responsible but the polarisation of the chromophoric group. Nevertheless this formulation is closer to the original theory of Hantzsch and Schæfer. The physical-chemist, on the other hand, is more inclined to treat the ionic form $H^+ + NO_3^-$ and the covalent one $H–O–NO_2$ as two entirely different molecules, each possessing its own characteristic absorption and consequently considers the deviation from the Debye-Hueckel theory or from Beer's law as a first order effect. Therefore he does not speak of the polarised anion but stresses more the causes of this polarisation by introducing a third electrovalent but associated form instead.

It is evident that both opinions differently expressed mean essentially the same and we have made these few remarks on the structure of nitric acid in solutions only in order to show, that these differences found in literature neither invalidate the empirical criterion for the covalent and the electrovalent linkage of the NO_3 group, (which is safely established by the two limiting cases without regard to concentrations of the acid of medium strength) nor the theory of the transition from covalent to electrovalent linkage with which we have to deal below.

This interpretation, and therefore also the spectroscopical criterion of the covalent and electrovalent bond of nitrates, is corroborated by measurements of the Raman effect,[16] showing that the electrovalent form is practically alone present in aqueous solutions up to 30% and that with higher concentrations the Raman lines of the covalent form appear and gain more and more in intensity.

It is interesting to note, that the transition from covalent to electrovalent linkage depends to a very high degree on the nature of the solvent. For aqueous solutions the absorption curve of nitric acid shows an abundance of the electrovalent form up to a concentration of 9.22 *m* whereas in a concentration of 14.8 *m* a high percentage of covalent molecules is indicated. If an acid is used as solvent even in a diluted solution a great number of covalent molecules may be present, if the concentration of the acid, used as solvent, is strong enough ; thus in $HClO_4$ a concentration of 0.15 *m* indicates already the characteristic form of the absorption curve due to covalent molecules, when the concentration of $HClO_4$ is about 7 *m*. In ether the same obtains even for a solution of 0.053 *m* of nitric acid, and in hexane the electrovalent form appears to be missing entirely. We shall see below, that this specific influence of the outside forces is in excellent agreement with the theory of the transition from covalency to electrovalency.

Similar conditions obtain for other acids and their derivatives. The sulphate ion, even in supersaturated solutions at 40° C. of Na_2SO_4 does not show any selective absorption at all, but an end-absorption only, just at the limit of the quartz spectrograph at about 225 $m\mu$. In solution of $NaHSO_4$ and $KHSO_4$ in strong concentrations, and in Na. CH_3. SO_4 in aqueous solutions a diffuse selective absorption has been found in the region between 300 and 250 $m\mu$, whose centre of gravity is difficult to determine accurately. When both bonds become covalent, *i.e.*, in dimethyl sulphate and diethyl sulphate, a similar but more distinct selective absorption obtains, the maximum in the liquid state and in ether solutions lying at about 275 to 270 $m\mu$.[17] We did not find any experiments described in the available literature on the absorption of similar substances in the vapour state but since the Raman effect indicates a high percentage of covalent molecules $(H—O)_2SO_2$ in aqueous solutions containing about 50% of sulphuric acid ($H_2SO_4 + 5H_2O$) we decided to take the absorption of the esters in the liquid state and of H_2SO_4 in the vapour state as criterion of the covalent form. The bands of selective absorption in solution have been found rather late, because their absorption coefficient is 1000 to 5000 times smaller than in the case of the nitrates and necessitates to measure the absorption of the acid in the vapour state with long columns of the absorbing substance. With a tube of 80 cm. length and 2 mm. vapour pressure we found selective absorption in the vapour of pure H_2SO_4 in the region between 290 and 260 $m\mu$ with a maximum at about 262 $m\mu$ resembling the absorption of the organic esters in contradistinction to the absorption of the sulphate ion.

Aqueous solutions of KNO_2 have been measured by v. Halban and Eisenbrand[11] and possess a distinct absorption maximum at 375 $m\mu$. In

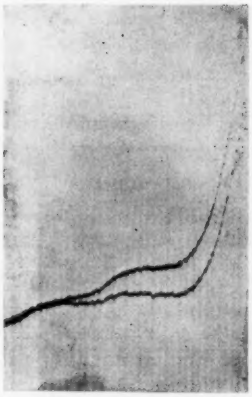


FIG. 1. KNO_3.

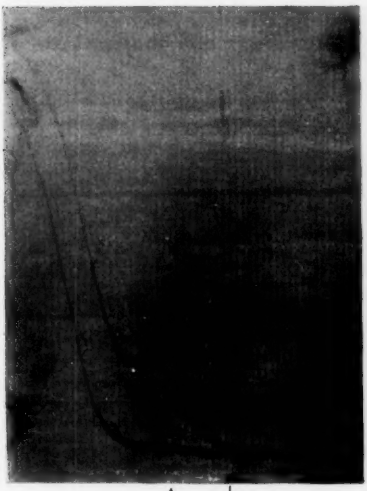


FIG. 2. $AgNO_3$.

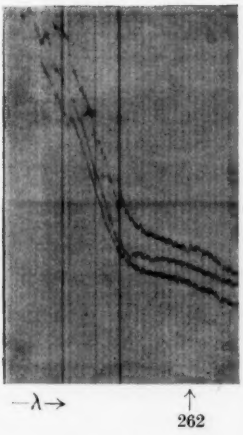


FIG. 3. $NH_4 \cdot NO_3$.

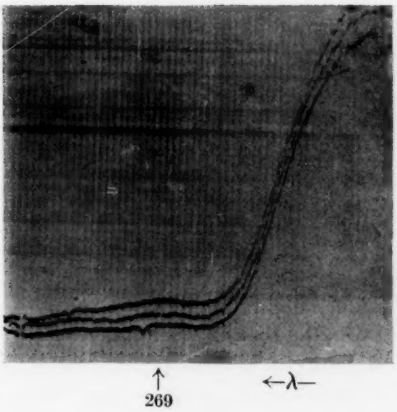


FIG. 4. $Zn \cdot SO_4$.

the vapour state[13] the maximum is again shifted towards shorter wave-length, *i.e.*, to 363 $m\mu$ in ethyl nitrite. This difference is, however, very small and it may well be that both maxima are identical, belonging to a photo-dissociation common to the electrovalent and the covalent form, and that the maximum is shifted on account of polarisation in solution.

Experimental.

The substances were heated in porcelain tubes of about 80 cm. length in order to obtain clear absorption spectra even with low vapour pressures, *i.e.*, at such low temperatures, where decomposition does not yet take place. The porcelain tube was closed on both ends by heavy brass fittings carrying a quartz window each, which allowed a connection with the vacuum arrangement and were surrounded by cooling spirals. The continuous hydrogen spectrum was used as the source of light and a small Hilger quartz spectrograph as the resolving instrument. Besides the standard lines (Cu arc) on each plate absorption spectra through the empty tube and through the vapour in vacuum were taken with equal times of exposure. These plates were measured by means of a recording microphotometer (see Figs. 1 to 4) and the position of the red wave limits and maxima determined directly on the photometer records.

After having placed the compounds in the absorption tube this was evacuated at room temperature for one to several hours, in order to remove the crystal water. This process was repeated for some hours at various temperatures in the range up to about 100° C. below the melting point of the anhydrous salt. Then the temperature was increased up to the melting point and above it, and the spectra taken.

The results are collected in Table I and Figs. 1 to 4 are reproductions of photometer records of KNO_3, $AgNO_3$, $(NH_4)NO_3$, and $ZnSO_4$. The spectra have been taken under the following conditions :—

Nitric acid, HNO_3—decomposes easily on heating. At 90° C. the bands of NO_2 can be seen on the plate and with slightly higher temperature also absorption bands of NO appear. The final plates have been taken after replacing the long porcelain tube in this case by a small silica tube of 10 cm. length, varying the vapour pressure at room temperature. The selective absorption appears at 2 mm. vapour pressure and is well developed at 4 mm.

Potassium nitrate (*M.P.* 336° *C.*).—The first of the two sets of NO_2 bands appears on the plates at the temperature of 475° C. At 360° C. to 375° C. selective absorption obtains which disappears at higher temperatures along with the appearance of the NO_2 bands (Fig. 1).

Silver nitrate (*M.P.* 208°.5).—Decomposition becomes rapid from 250° onwards, the selective absorption being well developed at 234° (see Figs. 1 and 2).

Magnesium nitrate—begins to decompose, according to the appearance of the NO bands, already at about 170°, the NO_2 bands appear at about 300°. The spectrum at lower temperatures (165°) shows rather an indistinct selective absorption which is better developed at 280° to 300° C.

Cadmium nitrate (*M.P.* 350°)—decomposes very rapidly. At 350° C. the two sets of NO_2 bands are already very strongly developed and fill almost the whole spectrum. The absorption spectrum of the vapour could not be obtained.

Lead nitrate, $Pb(NO_3)_2$.—The NO bands begin to appear at about 290°, those of NO_2 at 370°. The selective absorption of the vapour is present at 240° and is still better developed at higher temperatures.

Ammonium nitrate, NH_4NO_3.—The decomposition of ammonium nitrate occurs first at about 200° C. indicated by the NO_2 bands, and becomes very rapid at about 280° C. The selective absorption is indicated at about 110° C. and well developed at about 240° C. It was rather difficult, to maintain equal illumination, because water vapour was freely condensed on the quartz windows, but the same continuous absorption could be recognised on a great number of photometer records, taken from different plates (Fig. 3).

Sodium nitrate, $Na(NO_2)$ (*M.P.* 276°.9).—The decomposition is indicated by the appearance of the two NO_2 band systems, but it appears interesting that also the typical NO bands appear much stronger than in the nitrates. As a matter of fact, these latter bands begin to appear at about 275° C. whereas the NO_2 bands are appreciably developed at 380° C. only. At both these temperatures the selective absorption of the salt in the vapour state is already unmistakably present on the photometer record.

Sulphuric acid, H_2SO_4—is liable to rapid decomposition, when heated in the liquid state. The first SO_2 bands appear at about 110° C., they are fully developed at about 270° C. and the decomposition appears to be almost complete at 400° C. The final plates were taken by placing the acid in a side bulb, and by selecting various vapour pressures without heating it. The selective absorption is well developed on plates, taken with a 80 cm. tube and with 2 mm. vapour pressure. It appears, however, as if some SO_2 still was present, because with increasing temperature and pressure not only the red wave limit but also the maximum shifts considerably towards longer waves, between the limits of 290 and 260 $m\mu$. We believe that the long wave maxima are produced by the superposition of the absorption of unresolved SO_2 bands and from a careful study of a greater number of plates

and photometer records we think the value of 262 $m\mu$ the most probable one. Similar difficulties occurred in K_2SO_4 and these two values are therefore less reliable than those of other compounds.

Potassium sulphate, $K_2(SO_4)$ (*M.P.* 1067°).—The short wave SO_2 bands appear at 775°, the first of the near ultra-violet bands at 830°. The selective absorption of the salt is just indicated at about 600° and very well developed at about 800°. Here similar difficulties were encountered as in H_2SO_4, and the value of 254 $m\mu$ appears to be the most probable one for the maximum.

Silver sulphate, $Ag_2(SO_4)$ (*M.P.* 660°).—The first weak indications of the SO_2 bands appear already much below the melting point at about 180° and the decomposition becomes rapid at about 300° to 350°. Selective absorption of the vapour obtains from 160° onwards.

Zinc sulphate.—Decomposition obtains from 550° onwards and becomes very rapid from 800° onwards. The continuous absorption of the salt can be recognised from about 600° onwards, together with that of traces of SO_2 at longer wave-lengths (Fig. 4).

Ammonium sulphate—is very unstable and decomposes easily, so much so that already near the melting point the near ultra-violet SO_2 bands cover the region of the probable selective absorption. We have not been able to obtain a plate on which the selective absorption could be determined with complete certainty but some plates indicate that $(NH_4)_2SO_4$ behaves similar to K_2SO_4.

The Structure of Nitrates and Sulphates in the Vapour State and the Transition from Covalency to Electrovalency.

From Table I, where the results are summarised, it can be seen, that the figures are more or less the same for all the nitrates and all the sulphates respectively. Whether the individual differences from salt to salt are genuine or not is difficult to say at the present moment. It has been pointed out in earlier papers[3] that for continuous absorption spectra the position of the red wave limit, and to a smaller degree, that of the maximum depends on temperature and vapour pressure, and these two factors vary very much in these experiments for the different salts. For these salts the accurate determination of the wave-lengths of the maxima becomes even more difficult, because the vapour pressure obtainable without decomposition, is rather low and the maxima themselves naturally rather flat and further experiments with even longer absorption cells and higher resolving power are necessary. It can be seen, however, that the absorption of the sulphates generally lies on the long wave side of the nitrates and that in both cases

TABLE I.

	Beginning of Absorption	Maximum	Retransmission	Remarks
	λ ($m\mu$)	λ ($m\mu$)	λ ($m\mu$)	
$(NO_3)^-$		302		Nitrates in dilute aqueous solution[11,12]
(HNO_3)		~265		Nitric acid in hexane[11,12]
$C_2H_5NO_3$		~270		Ethyl nitrate in hexane[11,12]
$C_2H_5NO_3$		~265		Vapour[13]
HNO_3	298	262	252	Vapour, present paper
KNO_3	308	267	252	,, ,, ,,
$AgNO_3$	301	263	251	,, ,, ,,
$Mg(NO_3)_2$	294	270	257	,, ,, ,,
$Pb(NO_3)_2$	292	268	252	,, ,, ,,
NH_4NO_3	299	262	252	,, ,, ,,
$(NO_2)^-$		375		KNO_2, dilute aqueous solution[11]
$C_2H_5NO_2$		363		Ethyl nitrite, vapour state[13]
$NaNO_2$	301	271	254	Vapour, present paper
SO_4^-		< 225		Sulphates, in dilute aqueous solution, max. probably in Schumann-region[17]
$(CH_3)_2SO_4$		~275		Dimethyl sulphate, homogen. liquid[17]
$(C_2H_5)_2SO_4$		~270		Diethyl sulphate, homog. liqu. and sol. in ether[17]
H_2SO_4	285	262	254	Vapour, present paper
K_2SO_4	293	258	254	,, ,, ,,
Ag_2SO_4	300	265	250	,, ,, ,,
$ZnSO_4$	294	269	242	,, ,, ,,

the region of selective absorption is close to that of the organic esters but very different from that of the free ions in solution. We conclude, that inorganic sulphates and nitrates are covalently bound in the vapour state For the nitrites this is not yet certain, but probable.

To our mind this result is by no means surprising. The experiments of Franck and his collaborators[1] have shown that a transition from covalent to electrovalent linkage exists for the same molecule under different experimental conditions. Thus AgCl, well known to dissociate into Ag^+ and Cl^- ions in solution and in the fused state, possesses a covalent linkage in the vapour state according to its continuous absorption spectrum and its band spectrum in emission. Similarly HCl, HBr, and HI are covalently bound in the vapour state according to their absorption spectrum, their Raman effect and the value of their dipole moments.[18] There are only two possibilities to explain these results. We have either to assume the existence of a particular class of molecules, which dissociate adiabatically into ions but are not made up of ions in their ground state, or, we assume that the bond may change from the covalent to the electrovalent character. In order to leave both ways open, Franck put forward the terminology of atomic binding and ionic binding, mentioned above. If the first explanation would be found valid, the terms electrovalent and covalent could be preserved with their chemical meaning and could denote compounds, which dissociate into ions or which do not respectively. If the second explanation holds, any bond would be either electrovalent or covalent at a particular moment, the two terminologies becoming identical, but the nature of the same bond would be found different under different conditions. From the point of view of wavemechanics both explanations are possible.[19] The latter one, *i.e.*, the transition from covalent to electrovalent linkage would find its analytical representation in an increasing difference of the normalising factors of the bonding wavefunction, *i.e.*, in an increasing dissymmetry of the molecular fields. The first explanation can be described wavemechanically by hybridisation of several wavefunctions. The term hybridisation is used with different meanings in literature, and the type of hybridisation discussed here obtains, when the two potential curves involving ions and atoms, come near enough and perturb each other at such internuclear distances as really prevail in the completed molecule. An intersection of the ionic and the atomic curve at large internuclear distance, which was believed sometime ago to explain such cases, is not qualified to bring about a hybridised ionic-*cum*-atomic bond. But the theory itself is unable to decide, the order of magnitude for the dissymmetry of the fields or the energy difference of the electronic levels at the minimum position of the $u : r$ curves, necessary for the explanation of these phenomena. Experimentally, however, it can be said, that a hybridisation would mean a perturbation of the vibrational levels and it should be possible to recognise it in the band spectrum. Neither the bands of AgCl indicate a perturbation owing to the

hybridisation of the ionic and atomic potential curves, nor the bands of BeO, MgO, etc. for which hybridisation of the s and p terms was supposed for similar reasons. In all such cases the spacing of the vibrational levels is quite regular.

On the other hand it is clear, that the transition from covalency to electrovalency depends to a very high degree on external conditions. According to conductivity and Raman effect, AgCl is electrovalent already in the melted state, but HCl remains covalent in the liquid state in the absence of water and even in solution in solvents of smaller dipole moment. Thus the expected experimental evidence for the explanation of hybridisation is missing but that for the influence of external forces exists indeed and we believe, therefore, that the second explanation holds. We identify the definition of covalency and atomic binding on the one hand and of electrovalency and ionic binding on the other hand, but assume, that the nature of the bond may change for the same molecule under different conditions.

The influence of external conditions and forces on the nature of the bond may easily be seen from the Franck-Condon diagram. Here the different effects of polarisation can be considered by introducing the changes of energy produced by them. Fig. 5 contains the $u : r$ curve of KCl. The ground state of this electrovalent molecule dissociates into $K^+ + Cl^-$.

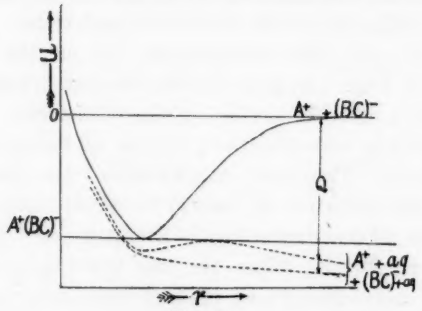


FIG. 5.

The level of the separated unexcited atoms K + Cl lies 0.6 volts (ionisation potential of K *minus* electronic affinity of Cl) below it and a flat repulsive curve originates from it, as can be seen from the red wave limit of its absorption spectrum in the vapour state. The thermochemical energy of formation $(K^+ Cl^-) \leftarrow K + Cl$ is 4.5 volts, the adiabatic dissociation energy $(K^+ Cl^-) \rightarrow K^+ + Cl^-$ is 5.1 volts. The energy of hydration is for the K^+ ion about 93 K.cal./mol., for the Cl^- ion about 89 K.cal./mol.,[20] together about 7 volts. The hydration energy of an undissociated electrovalent molecule $(K^+ Cl^-)$ is of course not known, but it is clear, that the field outside

such a molecule, in which the changes are counterbalanced, is much weaker, than that surrounding the separated ions. As a matter of fact, the dissociation of the molecule in solution proves, that the curve involving the separated hydrated ions ($K^+ + aq$) + ($Cl^- + aq$) is a repulsive one. The further question, whether a labile minimum position remains in the neighbourhood of the internuclear distance of the gaseous molecule ($K^+ Cl^-$) is of no interest here. It can be seen, however, that the level of the separated *hydrated* ions lies 1.9 volts below the ground level of the molecule. Almost the same obtains for AgCl in spite of this molecule being covalently bound in its ground state. The ground level and the excited level possess a dissociation energy of 3.1 and 0.3 volts respectively[21] according to its band spectrum,† the energy of

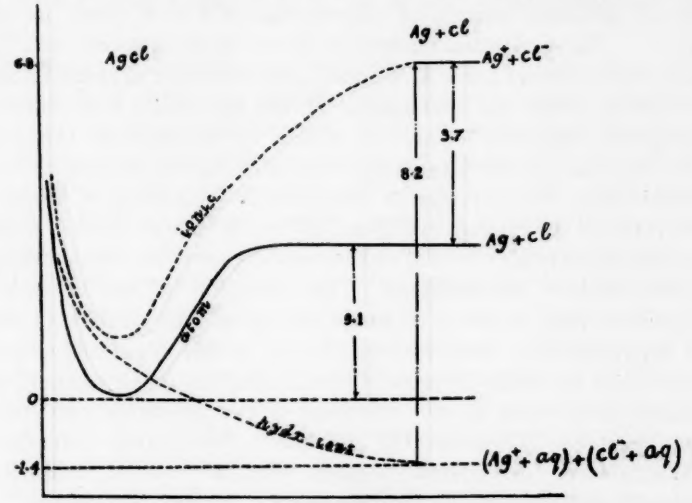


FIG. 6.

† Ag in the term d^9s^2 ^2D as dissociation product of the initial level was originally suggested by Brice, but such a term, about 1.9 volts above the ground state, is not yet known in the spectrum of Ag. One of us (R. Samuel, "Absorpt. Spectr., etc", ref. 2) has suggested another possibility, because the extrapolation from the Ag^+ spectrum would give 4.8 volts instead of 1.1 volts. The ^2D term is however known in the Cu spectrum where it lies 1.38 volts above the ground state ^2S and since the ionisation potential of Cu (7.68 volts) is slightly higher than that of Ag (7.54 volts), the term value of ^2D will be indeed very near to 1.1 volts. It appears that the extrapolation from the spectrum of the ion which gives good results for the extrapolation, *i.e.*, of the anomalous terms of the earth alkali metals (*cf.* W. Grotrian, "Graph. Darstellung, etc.", Berlin, 1927) cannot be applied to such configuration involving an excitation of an electron of the closed d^{10} configuration. The band spectrum of AgO (F. W. Loomis and T. F. Watson, *Phys. Rev.*, 1935, **48**, 280) confirms Brice's interpretations of the dissociation of AgCl.

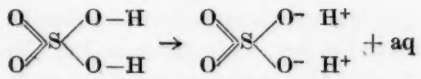
excitation of the molecule being 3.9 volts. But the level of the separated ions lies in this case much higher, about 3.7 volts above that of the normal atoms, because the ionisation potential of Ag is much greater than that of K. In spite of this, the level of the *hydrated* ions becomes again the lowest one of the whole system, the hydration energy of Ag^+ being 100 K.cal./mol.[20] that of Ag^+ *plus* Cl^- being 8.2 volts. The level of $(Ag^+ + aq) + (Cl^- + aq)$ therefore lies not only 4.5 volts below that of Ag + Cl but also 1.4 volts below the ground state of the covalent gaseous molecule (AgCl). Hence the curve involving the level of the separated hydrated ions intersects that of the ground state of the covalent molecule and becomes a repulsive one. The actual position of the ionic curve is not known, but since the radius of Ag^+ is slightly smaller than that of K^+ and its polarisability greater it will possess an adiabatic energy of dissociation of 5 to 6 volts, as indicated in Fig. 6. The hydration energy of the covalent molecule will be much smaller, of the order of a few K.cal./mol., and is entirely neglected here. These considerations make the mechanism of the transition from covalency to electrovalency perfectly clear. It occurs on account of the additional energies supplied by the interaction with surrounding molecules or ions in the liquid state, the energies of solvation or hydration in solutions, the lattice energy in the crystal, and these will be big enough, when the minimum of the ionic curve is near to that of the covalent potential curve, which forms the ground state of the molecule. This condition, as can be seen from a comparison of Figs. 5 and 6, depends mainly on the position of the level of the separated ions with respect to that of the separated atoms. The changes in the adiabatic energies of dissociation are much smaller but those introduced particularly by the variation of the ionisation potential of the positive partner. Therefore the difference, "ionisation potential *minus* electronic affinity" determines roughly, whether such a transition from covalency to electrovalency is possible or not. Indeed, Samuel and Lorenz[22] could show, that a great number of chemical phenomena as conductivities, hydrolysis, the character of an hydroxide as acid or base a.o., which are intimately connected with the transition from covalency to electrovalency, follow exactly this difference throughout the periodic system. In reality the molecule is rigorously homopolar, when the sum of the energies for all the electrons of the bonding orbital is equal for either of the nuclear fields, the polarity of the molecule is measured by a comparison of the sum of ionisation potential *plus* electronic affinity of both the atoms. But it is sufficient to compare either the ionisation potential or the electronic affinity because both change in the same sense.[19] It is of course possible to consider the reverse process, the transition from electrovalency to covalency in a similar

manner, *e.g.*, by the theory of deformation of Fajans. To our mind, however, the above manner appears to be more satisfactory from a logical point of view and also to be a closer approach to reality. This can be seen from the fact, that in the sub-groups of the periodic system the transition from covalency to electrovalency always occurs easier with molecules formed by the middle element, *e.g.*, Ag, Cd, In, than for those formed by *both* their neighbours Cu and Au, Zn and Hg, Ga and Tl.[23] In a series like Zn, Cd, Hg, those properties, which form the parameter of transition in the theory of deformation like the ionic radius (0.83, 1.03, 1.12 A.U.) and the polarisability of the ions (0.29, 2.44, 5.05) form a monotonous series, whereas the ionisation potential shows indeed a minimum for the middle element (first ionisation potentials = 9.4, 9.0, 10.4, second ones = 17.9, 16.8, 18.7 volts respectively for Zn, Cd, Hg).

The above considerations support the point of view taken up in this paper; such a transition is possible in the same molecule under different experimental conditions and therefore the terms of ionic and atomic binding and electrovalency and covalency respectively may well be identified. From the absorption spectra of diatomic halides Franck and his collaborators had concluded, that those of H and Ag are covalently bound in the vapour state, those of the alkali metals Na, K, Rb, and Cs indicating electrovalent bond. Since H and Ag possess a high ionisation potential, the alkali metals a low one, we expected a similar difference in the case of nitrates and sulphates, and, as far as the homogeneous acids are concerned, covalency was already established by the Raman effect. This is supported by experiments of Butkow[23], which show that triatomic halides are covalent in the vapour state like those of Zn, Cd and Hg, with high ionisation potential, but electrovalent, if the ionisation potential is low, as in those of Pb. But the experiments reported here show, that in this case even the alkali salts possess a covalent bond in the vapour state. This evidently is due to the electronic affinity of the nitrate and sulphate ion. Its exact value is not known, but it is clear, that it will be smaller in such a complicated system than for a simple halide ion. The above experiments indicate that the difference between the electronic affinity of the halides and these groups is considerable and greater than what could be expected.

As the absorption spectra in the vapour state indicate covalent bond between the metal and the oxygen atom for the nitrates and sulphates, it appears, as if this phenomenon is rather common and we expect most of the simple inorganic salts (as distinct from genuine complex salts) to behave similarly. Further experiments on this point are in progress. In current literature the sulphate or nitrate ion is often described by a formula

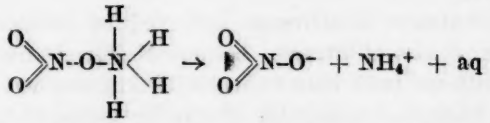
$[SO_4]^-$ and $[NO_3]^-$ indicating that such molecules belong to the same class of compounds as Werner's complex salts. It has been pointed out[24] that according to spectroscopical results several classes have to be distinguished among the complex salts, as the term is used to-day, and quite different mechanisms of linkage are responsible, *e.g.*, for the existence of NO_3^-, $[Cr\ (CN)_6]^{3-}$ and $[Cr\ (H_2O)_6]^{3+}$, each of them representing a different type of chemical union. Werner himself was the first to assume that the sulphate and nitrate ion are really complex salts, but, while it can be understood that he tried to extend his new theory of co-ordination as far as possible, it should not be overlooked, that the arguments put forward by him do not hold any longer. As a matter of principle he did not want to make use of particular and definite ideas on the structure of atoms and did not want to ascribe different states of valency to the same atom. To-day there is not the slightest difficulty to explain the tetra and hexavalency of sulphur on the basis of the configuration $s^2 p^4$ of the sulphur atom, the *s*-electrons being active in the hexavalent, but inactive in the tetravalent state. Again the experimental facts cited by Werner, do not warrant in themselves, the assumption of a co-ordinate bond for *e.g.* SO_4^{2-}. The hydrogen atoms are easily substituted in H_2SO_4, it is true, but this does not prove that they are bound in the second sphere of a complex, because the same is true for the hydroxyl group too, as can be seen from reactions like the combination of H_2SO_4 and HCl to give SO_2Cl_2. Indeed just for such cases Werner ultimately had to assume a rearrangement into " ordinary valence compounds".[25] To our mind the covalent bond in the vapour state indicates clearly that a description by the older structural formulæ



are a close approach to reality, showing that such compounds can exist with the same number of valencies once in the covalent and once in the electrovalent state. Whether the two kinds of oxygen atoms, bound with a single and a double bond in the covalent form still can be distinguished in the free ion or not is a different question. Electronic configuration for both cases are conceivable and a definite answer on this point cannot be given at this moment.

Particular interest attaches itself to the spectrum of ammonium nitrate which does not form an exception but absorbs similarly to the other nitrates. Sidgwick[26] has introduced the "covalency maximum" of four for nitrogen on the bisis of the Octet Theory and quotes the ammonium salts as examples, showing that the fifth bond of nitrogen cannot be covalent. Since $NH_4.NO_3$

in the vapour state absorbs like $C_2H_5.NO_3$ and not like the free nitrate ion in solution, there appears to be no other possibility but to describe it by a formula



according to which nitrogen possesses 5 covalent bonds in the vapour state and the bond with highest polarisation becomes electrovalent on account of the external energies of the lattice or of hydration. As to the nitro-group, it has been proposed to avoid the pentacovalency by the assumption of a resonance bond. For such a system, wavemechanical calculation becomes rather complicated, but for a similar case, *i.e.*, the $(HF_2)^-$ ion, quoted often along with the nitro-group in this connection, it can be seen at once, that a resonance linkage does not exist. For this purpose we assume for this ion a model, consisting of two F^- ions, bound together by a proton. This model corresponds exactly to that of H_2^+, made up of two H^+ ions, bound by a single electron, as it is used for wavemechanical purposes, only with the reverse signs. Therefore the results of the corresponding calculation[27] may be applied, and it can be seen, that the system $(FHF)^-$ indeed possesses a stable minimum position, like H_2^+; but because the proton is about 1840 times heavier than the electron, the dissociation energy of HF_2^- would be 1840 times greater and the internuclear distance (F—F) 1840 times smaller than the corresponding dissociation energy and distance in H_2^+. If a physical meaning is at all attached to such a calculation, it cannot be anything else but that of an " united atom ". At the internuclear distance of the $(HF_2)^-$ ion, the system accordingly does not possess a stable minimum position, produced by wavemechanical interaction.

On the other hand, the existence of this ion in solution is readily explained by electrostatic attraction between the dipole of non-dissociated HF molecules and F^- ions and such an explanation makes it easily understood, why such phenomena are always confined to the elements with smallest atomic dimensions, as has been pointed out elsewhere.[28] Also in this case ions like $(HCl_2)^-$ and $(HBr_2)^-$ do not exist. Resonance linkage is doubtless present in aromatic compounds, but because it accounts here for the particular aromatic properties, it is all the more probable *a priori*, that it does not exist in non-aromatic molecules, and it is therefore our view, that the nitro-group has to be conceived as derived from a pentacovalent nitrogen atom. As to the ammonium part of $NH_4.NO_3$ in the vapour state, there is little doubt, that nitrogen is pentacovalent according to the absorption

spectrum and this agrees with recent indications of a pentacovalency of N in solutions of tetra-alkyl ammonium salts[14] and certain evidence for the existence of NF_5.[29]

The pentacovalency of nitrogen, indicated for ammonium nitrate in the vapour state, is also of interest, because Mulliken[30] uses the existence of the NH_4 ion with not more than 4 covalent linkages as a general argument, to interpret the method of molecular orbitals by means of the identification of non-premoted and bonding electrons as a theory of valency in which the single electron possesses bonding power. The above results favour directly an electron pair-bond theory of valency, as suggested elsewhere,[6,28] and may be added to the increasing spectroscopical evidence, which supports this view.

Discussion of Possible Photo-dissociation Processes.

The correlation of the maxima observed in the vapour state and their red wave limit to particular processes of photo-dissociation meets with two difficulties. Firstly, as in all experiments concerned with continuous absorption spectra, it is difficult to determine the red wave limit belonging to the vibrationless molecule. As discussed elsewhere in some detail,[3] the observed red wave limit will give too large values of the dissociation energy if the number of absorbing molecules is not sufficient to make the absorption complete, and it will give too small values, when a considerable percentage of the absorbing molecules is already excited to higher vibrational levels of the ground state, the number of collisions being increased by increased pressure or temperature. In this particular case the vapour pressure of the anhydrous salts is particularly small and we have tried to account for that by an absorption tube of unusual length. The difference between the observed maxima and the red wave limit is generally about 300 A.U., and according to experience gained with other substances, such a figure should give a value not too much different from that of the vibrationless molecule. We believe, that the dissociation energies obtained from the beginning of the continuous absorption will be of the right order of magnitude, and, if anything, rather too great than too small.

The second difficulty is the following : all inorganic nitrates in aqueous solutions of low concentration show the same selective absorption $\lambda_{max} = 302\ m\mu$, which evidently has to be correlated to some process of photo-dissociation of the NO_3^- ions. Nitric acid in highly concentrated aqueous solutions, in non-dissociating solvents, organic nitrates in solution are measured as homogeneous substance, and all inorganic and organic nitrates in the vapour state exhibit the same selective absorption with its centre of gravity at about 265 to 270 $m\mu$; this evidently has to be correlated to some

photo-dissociation of the covalently bound NO_3 group, since otherwise the above figure could not remain rather constant for so different partners as Na, H and C_2H_5. Hence the transition from electrovalent to covalent linkage brings about a change in the dissociation process in such a way, that the dissociation energy is *increased*. In a similar way there exists some dissociation process for the sulphate ion with a red wave limit at 220 $m\mu$ or below. Organic sulphates in the liquid state or solution, sulphuric acid and inorganic sulphates in the vapour state all possess a selective absorption $\lambda_{max} = 270$ to 290 $m\mu$. Similarly this has to be ascribed to a dissociation process concerning the covalently bound SO_4 group, and the transition from electrovalency to covalency in this case brings about a change of the dissociation process which *decreases* the dissociation energy. But in both the groups, NO_3 and SO_4 in covalent linkage we have a central atom bound to oxygen atoms according to its maximal number of valencies and hence we should not expect dissociation processes, which are vastly dissimilar.

It could be possible to account for the above difference in behaviour, assuming that the spectra due to the negative nitrate and sulphate ions correspond to a dissociation process concerning not an atom but the superfluous electrons and are correlated to the electronic affinity of these ions. But then the electron affinity of *e.g.*, SO_4 would be greater, not smaller than that of iodine. Moreover, Krishnan and Guha,[31] have made it probable, that the two selective absorptions of the nitrate ions belong indeed to the two processes $NO_3^- \rightarrow NO_2^- + O(^3P)$ and $NO_3^- \rightarrow NO_2^- + O(^1D)$. Since they have taken the value of the red wave limit from absorption spectra in solution, the agreement between thermochemical determination and this value is not a definite proof, the beginning of the photo-dissociation of the free ions in the state of minimum vibration probably lies at higher energy values than they suppose, the potential curve of the repulsive state which is the final level of this transition, running rather steep towards decreasing internuclear distance. That the red wave limit lies at higher values of the absorption coefficient than those selected by Krishnan and Guha, can be seen from a comparison of the absorption spectra of many compounds in the vapour state and in solution, but nevertheless, the above correlation is made quite plausible, because the energy difference between the two maxima of NO_3^-, *i.e.*, 302 and 193 $m\mu$ is about 2.3 volts in fair agreement with the excitation energy 1.9 volts of $O(^1D)$, and the energy difference of the maxima is always more reliable than that of the red wave limits. They calculate for the dissociation process $NO_3^- \rightarrow NO_2^- + O(^3P)$ the energy difference of about 83 K.cal./mol. in dilute aqueous solution.

As to the absorption spectra of the covalent molecules, it is by no

means possible definitely to decide on the photo-dissociation connected with them. The known energies of formation of acids and salts cannot be used to calculate the atomic heat of formation, because they all refer to measurements in the crystalline state or in solution, in which these corresponds possess an electrovalent bond. Furthermore, it is not possible to calculate the atomic energy of formation from these values by means of some cycle, because a number of the necessary quantities, *e.g.*, the electron affinity of NO_3 are not known.

Atomic energies of formation of similar covalent molecules are, however, available for organic esters of nitrous and nitric acids, *i.e.*, for ethyl nitrite and ethyl nitrate, which can be calculated from the known heats of combustion. These are for the gaseous molecules 324 and 334 K.cal./mol. respectively. When calculating the atomic energies of formation and deducting one from the other, again all quantities cancel out with the exception of $\frac{1}{2}D(O_2)$ and hence the dissociation process $C_2H_5.O.NO_2 \rightarrow C_2H_5.O.NO + O$ represents an energy of $10 + 59 = 69$ K.cal./mol. The same value obtains for the anhydride of nitric and nitrous acid. The energies of formation from the elements are $Q(N_2O_5) = -1.2$, and $Q(N_2O_3) = -22$ K.cal./mol. and give the atomic energies of formation $D(N_2O_5) = 463$ and $D(N_2O_3) = 325$ K.cal./mol. or 69 K.cal./mol. for the dissociation process $\frac{1}{2}N_2O_5 \rightarrow \frac{1}{2}N_2O_3 + O$.

The dissociation process $SO_4^- \rightarrow SO_3^- + O(^3P)$ may be considered in a similar way. The following figures in Table II are obtained by adding half of the dissociation energy of O_2 to the heat of formation $Q(M_2SO_4)$ of the sulphates from the elements in aqueous solutions and deducting the corresponding heat of formation of the sulphites $Q(M_2SO_3)$:—

TABLE II.

M =	Na	K	NH_4	Mg*
$Q(M_2SO_4)$ ..	328	334	280	302
$+ \frac{1}{2} D(O_2)$ ..	59	59	59	59
$- Q(M_2SO_3)$ ..	264	275	214	240
$SO_4^- \rightarrow SO_3^- + O$ ..	123	118	125	121

* These figures refer to the solid state.

The atomic heat of formation of SO_2 has been calculated to 247, that of H_2O to 217 K.cal./mol. The heat of solution of SO_2 + aq is about 6 K.cal./mol., and the atomic heat of formation of H_2SO_3 in dilute aqueous

solutions comes to about 470 K.cal./mol. The heat of formation from the elements of 214 K.cal./mol. of sulphuric acid in dilute aqueous solution gives an atomic energy of formation of 607 K.cal./mol., and the dissociation energy of the process $H_2SO_4 + aq \rightarrow H_2SO_3 + aq + O$ is about 137 K.cal./mol. This value is slightly higher than that obtained from the salts, and the difference may be due to different degrees of dilution. It is, however, not impossible, that sulphuric acid behaves slightly different from the sulphates, because also in the vapour state the spectrum of the acid is slightly shifted against that of the salts. For the splitting off of a neutral oxygen atom from the free SO_4^{2-}-ion we may take an energy value of roughly 125 K.cal./mol. This corresponds to a wave-length of $227 m\mu$. The absorption of the sulphate ion indeed begins in this region and appears to be correlated to this process.

For covalent molecules of this type the corresponding energies cannot be calculated, because reliable values of energies of combustion of organic esters of sulphuric and sulphurous acids are not known. For the anhydrides of the acids from the values $Q(SO_3) = 92$ and $Q(SO_2) = 71$ K.cal./mol. by the addition of $\frac{1}{2} D(O_2)$ a value of 80 K.cal./mol. is obtained for the splitting off of an oxygen atom in the gaseous state. In analogy to ethyl nitrate and ethyl nitrite this value may be taken as valid for the organic esters provisionally.

In other words, the energy of this dissociation process is reduced from 125 K.cal./mol. for the hydrated ion to 80 K.cal./mol. for the gaseous covalent molecule. While the first value agrees with the beginning of the absorption spectrum in aqueous solution, the latter one corresponds fairly well to the red wave limit of sulphates and sulphuric acid in the vapour state. The mean of the above observations is about 90 K.cal./mol. and the difference of 10 K.cal./mol. is not significant in any way, because, firstly, the vapour pressure naturally was very small and, secondly, the upper repulsive potential curve runs parallel to the abscissa of the internuclear distance of the $U : r$ diagram only in rare cases. The above figures explain why the absorption is shifted towards longer wave-length in the transition from electrovalency to covalency and it appears, as if the beginning of the absorption has to be correlated to the dissociation of an unexcited O atom in both cases.

For the nitrates, however, the difficulty which was mentioned above remains, *i.e.*, that the absorption is shifted to shorter wave-length by the same transition from electrovalency to covalency contrary to the behaviour of the sulphates, while the energy of the dissociation process is decreased from 83 to 69 K.cal./mol. respectively, in a similar manner, as in the case of the sulphates. This may be explained, of course, by a different slope of

the repulsive curve. We know indeed a large number of polyatomic molecules, *e.g.*, the type CH_3Cl, where the energy of dissociation, measured optically, is much too large on account of the steepness of the upper potential curve. It should be borne in mind, that the energy differences measured by the red wave limit of the continuous absorption spectrum in reality are energies of electronic excitation of the molecule, which depend on the potential curve not only of the ground state but of the final state as well. But still, this disagreement is by no means satisfactory, particularly considering the good agreement obtained for sulphates, and since various other photodissociation processes are possible, a definite correlation of the red wave limit of the absorption in the gaseous state may be reserved for a time, till more experimental data of other inorganic salts are available.

Again the second red wave limit, *i.e.*, the point of retransmission, cannot be explained satisfactorily at present. The energy difference between the first and second red wave limit is about 0.8 volts for the nitrates and about 1 volt for the sulphates, and these values do not agree either with the term difference $^1D - {}^3P$ of oxygen or with its triplet separation. The difference between the absorption maxima which is not yet known, would give clearer results and also the discussion on this question has to be postponed.

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